

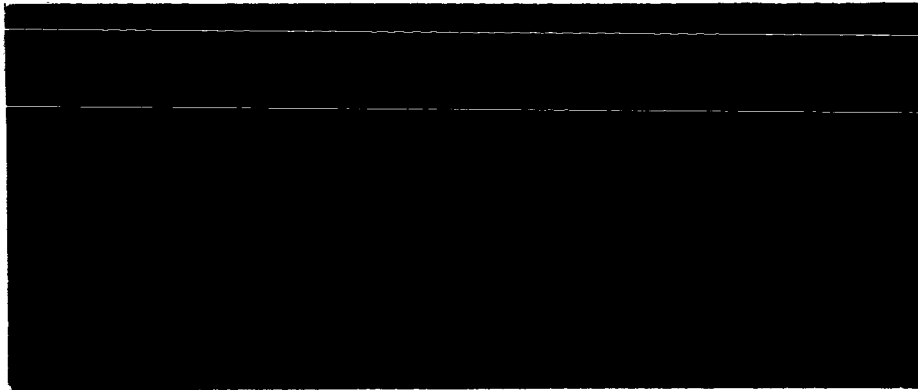
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CHEMICAL RESEARCH & DEVELOPMENT CENTER

FMC CORPORATION

PRINCETON, NEW JERSEY

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A STUDY OF THE FEASIBILITY OF THE  
REGENERATION OF CARBOHYDRATES IN A  
CLOSED CIRCUIT RESPIRATORY SYSTEM

Final Report  
(NASA Contract NASr-88)

(NASA CR ---) OTS:

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March 1, 1963

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A STUDY OF THE FEASIBILITY OF THE  
REGENERATION OF CARBOHYDRATES IN A  
CLOSED CIRCUIT RESPIRATORY SYSTEM

ABSTRACT

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A study has been made of the feasibility of producing formaldehyde from carbon dioxide. The process developed is carried out in two steps. In the first one, carbon dioxide is reduced with excess hydrogen in a glow discharge to the monoxide; in the second, the monoxide formed is reacted at ordinary temperatures with the remaining hydrogen in a silent discharge to give formaldehyde. A degree of conversion of the carbon dioxide of the order of 90% is easily attained. However, at somewhat lower degrees of conversion the power yield is several-fold higher. To produce one pound of carbon monoxide about 4 KWH are required. The yield of formaldehyde per unit of time increases steadily with increasing surface area covered by the discharge, the gas flow rate, the power input and the intensity of an impressed magnetic field. Indications of an approach to a maximum yield were not observed. It seems probable that power yields of the order of 50 grams of formaldehyde per KWH dissipated should be attainable using a reactor of adequate size and moderate recycling of the gas.

A large laboratory unit has been built and tested for the continuous production of formaldehyde from carbon dioxide and hydrogen in a closed system at steady state. Two different types of silent discharge reactors were built for this pilot plant. Both were designed to come within a factor of two or three of the size required for a closed respiratory system with a crew of five.

A mathematical analysis has been made of the design for a tapered, tubular spinning silent discharge reactor to operate at weightlessness with continuous feed of gas and liquid phase for absorption of formaldehyde generated.

Sugars have been made by the condensation of aqueous formaldehyde using calcium hydroxide and solutions of lead oxide in sodium hydroxide as condensing agents. A process has been developed which will generate sugars on a continuous basis.

The synthetic sugars were fermentable in part by yeast but were toxic to experimental animals when fed either by intubation or in a diet. No improvement in the material was obtained either by various fractionation techniques or by the alternative methods of preparation.

Analysis of the sugar mixtures has shown them to be complex and to contain at least thirteen different sugars. The nature of the toxic materials has not been elucidated but some compound or compounds other than formaldehyde, are believed to cause the toxicity.

*AUTHOR*

### RECOMMENDATIONS

Future work should be concerned initially with a study of the value of formose sugars as food, determination of the cause of the encountered toxicity in weanling rats, the degree of toxicity in other animals, and establishing a means of producing a non-toxic sugar. An essential part of the study should be a study of process variations and the catalyst used to effect the sugar formation. Concurrent with the above, work on formaldehyde formation should continue to establish optimum conditions for integrated operation starting from carbon dioxide to carbon monoxide and subsequent formaldehyde formation. Alternate methods of preparing formaldehyde also should be evaluated.

PART I

THE GENERATION OF FORMALDEHYDE FROM CARBON  
DIOXIDE AS A ROUTE TO EDIBLE SUGARS

by G.C. Akerlof

## CHAPTER 1. INTRODUCTION, EQUIPMENT AND PRELIMINARY DATA

### Introduction

This report covers one years investigation on the feasibility of recycling waste carbon dioxide and water back to edible foods for ultimate use in space travel. The concept was originally proposed by G.C. Akerlof at the ARDC Symposium on Closed Circuit Respiratory Systems, held in April of 1960. This concept was presented in more detail at the XIth International Astronautical Congress in Stockholm, 1960, "Food to Food Process Cycle for Extended Travel in Space" (Proceedings, pp. 598-606).

#### I. Purpose of Project

The feasibility of regeneration of carbohydrates during travel in space from the waste carbon dioxide and water has been undertaken for the purpose of developing a closed circuit respiratory system. Carbohydrates are able to supply up to 80% of our energy requirements and their regeneration at steady state would thus make it possible to extend space travel and visits to neighboring planets over periods of time of considerable length.

#### II. Chemical Reactions to be Used

Most organic matter present in food yields carbon dioxide when digested. When this substance is reduced to carbon monoxide, the latter may readily be reacted with hydrogen to give formaldehyde. Catalysts are available that will condense formaldehyde to carbohydrates that with or without inter-conversion in the body should be acceptable as food.

### III. Method of Approach

Assuming that the energy required for the conversion of carbon dioxide to yield carbohydrates would be available at steady state as electric power at voltages and frequencies suitable for the purpose, a four step method of synthesis is visualized:

#### A. Isolation of the Carbon Dioxide as a Pure Gas

It is recognized that CO<sub>2</sub> must be isolated as a pure gas prior to conversion to carbohydrates. Methods exist for this isolation and therefore will not be treated during this phase of the work.

#### B. Conversion of Carbon Dioxide to Monoxide

A considerable excess of electrolytic hydrogen is added to the dioxide and the mixture is passed through either a high temperature glow or a low temperature silent discharge. The former would give a high power yield and a high degree of conversion to monoxide per pass but low operating pressures and fairly high voltages are needed. The silent discharge gives a much lower degree of conversion and requires a considerable amount of recycling but would normally be run at about atmospheric pressure. There are, however, various approaches available for raising the power yield of the silent discharges which also would lower the recycle rate.

Perhaps it should be pointed out that the reaction under discussion will take place at a measurable rate at high temperatures in the presence of a catalyst. However, even in a glow discharge where, in comparison, reaction rates generally are extremely high and the residence time of the gas is measured in a few milliseconds, moderate changes of the length of the reaction zone have a large influence on the degree of conversion.

We are not concerned directly with the design of the electrolytic cell to be used for the generation of hydrogen and oxygen. May it suffice to say that it must be able to spin to be operable at weightlessness. It is conceived to consist of a number of thin segments arranged radially and containing alternate positive and negative electrodes separated by narrow conventional type diaphragms. The gases liberated are led out through manifolds connected with opposite ends of the hollowed out center shaft.

C. The Reaction of Carbon Monoxide with Hydrogen to Give Formaldehyde

Assuming a glow discharge is used for the conversion of carbon dioxide to the monoxide, the gas mixture formed is passed directly into a silent discharge where formaldehyde will be produced. A high power yield is probably attainable but formation of small amounts of methanol and various hydrocarbons should be anticipated together with partial polymerization of the formaldehyde produced which may give various carbohydrates. To prevent the formation of a solid layer of condensation products on the walls of the reactor it probably will turn out to be necessary to use a tapered, spinning reactor enabling a thin layer of water passing through to dissolve all formaldehyde generated. A preliminary design has been completed for such a reactor allowing continuous introduction and withdrawal of a liquid phase and recycling of the reacting gases while operating at weightlessness.

D. The Condensation of Formaldehyde in Aqueous Media

As already indicated, some degree of polymerization of formaldehyde may occur in a silent discharge. The occurrence of such reactions, their extent and the nature of their end products should be studied in detail. However, as is well known from data given in the literature, it is also possible to condense formaldehyde in its aqueous solutions in the presence of various catalysts like the alkali and alkali earth hydroxides.

IV. Reactors Assembled for the Study

A. Glow Discharges

In Figure 1 is shown a photograph of the glow discharge reactor assembled for the study of the conversion of carbon dioxide to monoxide. The upper electrode consists of a one inch diameter rod of dense graphite. The lower one is made of thin copper, formed as a blunt nose cone and efficiently water cooled. To quench the exit gases they have to pass through eight vertical quarter inch holes drilled through the water cooled base for the electrode. To reduce heat losses from the discharge, two co-axial Vycor tubes were placed inside the three inch Pyrex pipe forming the outside shell.

### B. Silent Discharges

Figure 2 illustrates the design of the silent discharge reactor. It consists mainly of an outer steel tube of 2" ID with an inner, co-axial glass tube of 1-5/8" OD packed in vacuum tight and filled with a dilute salt solution. Immersed in the salt solution is a water cooled, cold finger reaching down to the bottom. It is held in place by a Teflon fitting and serves to connect with the HV source. The amount of power dissipated is generally quite low due to the small power factor of the circuit employed. Operation over a period of several hours at a power input of 600-700 watts as uncorrected for the power factor makes the steel mantel tube feel faintly lukewarm.

Figure 3 shows in the center a reactor that is essentially identical with the one shown in Figure 2 except that it is appreciably shorter and the mantel tube is glass coated on the inside. By coupling them in series some idea of the effect of the size of the active surface area may be obtained. The reactor in the foreground of Figure 3 is mounted on a 6" Pyrex cross and enclosed by a 38" long solenoid made of thin copper strip. The solenoid has a resistance of about 5 ohms and is able to dissipate safely the heat generated by a current of 20 amperes at 100 volts but to keep its temperature down a high capacity blower is mounted on the Plexiglas flange covering one of the horizontal arms of the glass cross. The flange covering the opposite arm is drilled in the center for the reactor exit tube. The reactor itself is made entirely of glass and no ferromagnetic material is present inside the solenoid.

A magnetic field tends to change the shape of the path of an electron moving in an electric field. After an atomic collision an electron regains its kinetic energy over a distance of a few mean free paths. Any change in the length of the path traveled by the electrons may thus have an effect on the rate of a chemical reaction taking place in an electric discharge in the presence of a superimposed magnetic field.

The third reactor shown in Figure 3 was built for rough measurements of the effect of temperature changes on the amount of formaldehyde produced in a silent discharge. It will also allow the study of effects of changes in the condition of the surface of the center metal



electrode. The one shown in the photograph has a smooth polished surface but another one with a number of deep, square longitudinal grooves is also available. Both of them may be water cooled and in addition a liquid phase may be introduced together with the gas stream near their top ends through a number of small holes drilled close to the periphery of the adapter holding the electrode in place.

C. Flow Control for the Reactors

Figure 4 shows the control panel for the gas flow system. It serves without re-piping all the reactors already described and two more as well. Figure 5 illustrates a reactor operating with a liquid phase as ground electrode and Figure 6 gives a diagram of its design. During the course of an earlier study it was found that a similar reactor under certain definite conditions was able to give extraordinarily high power yields for the formation of peroxymonosulfuric acid. Even though the study of its use for our purposes is a shot in the dark, in accordance with the discussion given above of the use of a liquid phase to absorb formaldehyde generated in a silent discharge, data obtained with this reactor may yield the answer to several questions of importance.

D. Corona Discharge

Figure 7 illustrates a reactor that operates with a type of corona discharge. Thin perforated brass sheets with 330 holes per square inch are separated by Plexiglas rings and Teflon gaskets held together by micalex end plates. The current is a function of the voltage impressed and the distance between the brass plates. The reactor is light and strong but even at relatively high voltages of, let us say 18 KV, only weak currents of a few milliamperes are obtained.

V. Power Supply and Instrumentation for the Silent Discharges

A. High Frequency Generator and Associated Equipment

The electrical equipment employed for the operation of the silent discharge reactors consists of the following units:

1. Motor generator; type used gives an output of 1200 watts at 110 volts with a frequency of 1500 c.p.s.
2. High voltage, high frequency transformer. A specially designed 3 KVA transformer for a maximum of 40 KV is being used.
3. Electrostatic voltmeter, quadruple range, 0-30 KV.
4. Leeds and Northrup 10 point multiple instrument switch.
5. General Radio Variac, type M-2 gang for high frequencies.
6. Weston RF type milliammeters covering a wide current range.
7. Weston RF voltmeter and ammeter for Variac primary current.

A Dumont Model 411 dual trace oscilloscope with camera and other accessories may be available for short periods of time making it possible to obtain at least a few measurements of the power factor of the discharge circuits for the different reactors described above.

In Figure 8 is shown a diagram of the electrical circuit. From a purely electrical point of view, the silent discharge reactors may be considered to act as condensers as indicated in Figure 9. To maintain an electric discharge in the annular space of the reactor an alternating electromotive force of sufficient magnitude to ionize the gaseous dielectric must be applied. A low voltage 1500 c.p.s. current is generated by the motor driven alternator and supplied to the primary of the high voltage transformer through the General Radio type M-2 variac. The voltage across the reactor is measured with the electrostatic voltmeter and the current with Weston RF milliammeters in series with the reactor ground lead through the multiple point switch.

### B. Measurement of Power Factor

When an AC voltage is applied to a capacitor it is known that the current I leads the voltage E by  $90^\circ$  when no ohmic resistance is present. Since the silent discharge reactor essentially represents a capacitance a phase difference will exist between I and E. This phase shift or power factor must be known in order to get a valid power yield for the products formed in the reactor. The power W dissipated in the reactor is given by the expression:

$$W = E \times I \times \cos \phi \text{ watts}$$

where  $\phi$  is the phase angle between E and I. The out of phase or "wattless" power in the system is not lost but merely stored during one part of the cycle and returned during the rest of the cycle and has no relationship to the power actually consumed in the circuit. The measurement of the phase angle in a system like the one considered operating at high voltages and low currents cannot be accomplished using conventional electro-dynamometers or wattmeters. The most successful measurements of phase angle in cases like the one discussed have been made with a dual beam oscilloscope. The Dumont Model 411 oscilloscope referred to above uses a  $10^8$  ohms non-inductive voltage divider in series with a  $1.5 \times 10^6$  ohms measuring resistor to sample the voltage across the reactor. This voltage is applied to one of the Y-axis amplifiers of the oscilloscope. A 10 ohm non-inductive resistor in series with the low potential side of the discharge circuit is used to sample the current through the reactor. This voltage which is proportional to the current is applied to the other y-axis amplifier of the oscilloscope. The two traces obtained are superimposed vertically over each other and scanned simultaneously with a triggered, calibrated sweep. Usually the current signal is set to trigger the sweep, when it is leading the voltage. Figure 10 represents a photograph of a typical current-voltage trace obtained with the glass coated steel tube reactor described above. The phase angle may be computed directly using readings from the trace. By employing a calibrating sweep each space between the vertical lines represents in this case 100 microseconds. The time interval between the maxima of the current and the voltage peaks is measured and

divided by the time required for a complete cycle to occur. Multiplying the fraction obtained with 360 gives the phase angle. The traces of the oscilloscope also show whether the current leads or lags with respect to the voltage.

To tune a circuit containing a silent discharge reactor to resonance would be complicated due to changes in its resistance at the same time it is a capacitor. However, it is reasonably certain that sufficient tuning can be accomplished to obtain a considerable increase in the power factor, but a value close to unity is out of the question and also unimportant to our immediate purposes.

#### VI. DC Power Supply for Glow Discharges

This was a standard model F6005-AIK from Precision Measurements, Inc., which was designed to deliver currents up to 1 ampere at voltages of 0-5 kilovolts. The control circuit operates with a series regulator type 889-A power tube for a plate dissipation of 10 KW. The grid bias voltage is controlled with a General Radio type 1205B adjustable regulated power supply adopted for the purpose. A series of milliammeters allowed the measurement of output current using four different ranges. The power tube is cooled on the outside from above with an air blower and on the inside with water passing through 50 feet of half inch glass tubing on both sides.

#### VII. Some Preliminary Experimental Data

##### A. The Conversion of CO<sub>2</sub> to CO in a Glow Discharge

The equilibrium constant  $K_1$  for the reaction between CO<sub>2</sub> and hydrogen to give CO and H<sub>2</sub>O has been computed with high accuracy for a large temperature range by L.S. Kassel (J. Amer. Chem. Soc. 56, 1838, 1934) using spectroscopic data to obtain the thermodynamic functions required. Assuming  $K_1$  to be defined by the expression:

$$K_1 = \frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}}$$

the curve for the variation of  $\log K_1$  with temperature has been plotted in Figure 11. As shown by this curve the value of  $K$  increases very fast with the temperature. To obtain a high degree of conversion of  $\text{CO}_2$  to  $\text{CO}$  in an electric discharge a high operating temperature must be attained. In Tables 1 and 2 are given some preliminary experimental data verifying this conclusion. Using a glow discharge at a pressure of about 26 mm Hg and an electrode separation of 20 cm, up to 80% of the carbon dioxide present in the gas stream was converted to the monoxide with a power yield of about 110 grams of  $\text{CO}$  per KWH consumed. However, the yield was found to decrease considerably with increasing pressure and smaller electrode separation. By raising the voltage across the reactor, increasing the electrode separation to, let us say 25 cm, and decreasing radiation heat losses a little further, it would appear to be possible to obtain conversion of carbon dioxide to the monoxide about 80% per pass with only a minor increase in power consumption.

Some support for this conclusion is given by the data in Table 3. Assuming that a rapid approach to a true equilibrium takes place at the high temperatures generated in the glow discharge, and in view of the minute amounts of carbon dioxide that were found to form from the monoxide in presence of excess hydrogen, it would seem possible to attain conversions of  $\text{CO}_2$  to  $\text{CO}$  of the order of about 90%.

A calculation of the amount of carbon dioxide passing through the reactor for 24 hours at a flow rate of 4 liters per minute and ultimately converted to carbohydrates may be of some interest. Assuming a  $\text{CO}_2$  conversion to monoxide of 80%, a monoxide conversion to formaldehyde of 70% and a carbohydrate yield from formaldehyde also of 70%, the amount of formose sugar produced per 24 hours would be:

$$\frac{4 \times 60 \times 24 \times 30}{22.4} \times 0.8 \times 0.7 \times 0.7 = 3024 \text{ grams}$$

If one man per 24 hours produces 960 grams of carbon dioxide and 80% of this quantity were derived from formose sugar a reactor of a size even somewhat smaller than the one presently employed would be sufficiently large for the carbohydrate needs of a crew of five.

B. The Conversion of  $\text{CO}_2$  to  $\text{CO}$  in a Silent Discharge

As stressed above, in order to get a high degree of conversion, a high operating temperature is essential. The silent discharge reactors were originally set up to be used at ordinary temperatures but it was of interest to determine what degree of conversion was obtainable under these conditions. The data in Tables 4 and 5 show that conversions of an order of only 1% were attained with an average power yield of about 20 grams of carbon monoxide formed per KWH dissipated, in the case of the reactor with the mantel tube glass coated on the inside. The longer reactor gave essentially identical average power yield and degree of conversion. The temperature coefficient of the rate of conversion is unknown and cannot be estimated for the operating conditions given. Thus, some further measurements have been made at temperatures of about  $94^\circ\text{C}$  which have been summarized in Table 6. To obtain data at higher temperatures the mantel tube was wrapped with asbestos paper, two concave 100 watt chromalox heaters were clamped against the asbestos and then covered with several layers of the same materials. To record the temperature, two insulated thermocouples were packed against the surface of the mantel tube about three feet apart. As shown by the data in Table 6 there is no appreciable differences in degrees of conversion at ordinary temperatures and  $94^\circ\text{C}$ .

To summarize the results obtained from the preliminary data on the conversion of carbon dioxide to monoxide in a glow discharge, a high operating temperature is essential to obtain high yields. The residence time of the reacting gas in the plasma of the discharge needs to be only a few milliseconds per liter of gas, allowing the use of a small reactor at considerable flow rates. Conversions above 80% per pass should be obtainable at a power consumption of about 4 KWH per pound of monoxide produced. Operating at ordinary temperatures carbon dioxide may also be converted in a silent discharge to the monoxide, but the yield per KWH dissipated is much lower.

C. The Formation of Formaldehyde from  $\text{CO}$  and  $\text{H}_2$

The equilibrium between the components of this system has been studied experimentally by Newton and Dodge (J. Amer. Chem. Soc. 55, 4747, 1933). They obtained the following expression for the value of

the equilibrium constant,  $K_2$ :

$$\log K_2 = \log \frac{P_{\text{CH}_2\text{O}}}{P_{\text{CO}} \times P_{\text{H}_2}} = \frac{1710}{4.573T} - 5.431$$

where  $T$  represents the absolute temperature. Not only is the value of  $K_2$  small already at ordinary temperatures, but as shown by the curve for the value of  $\log K_2$ , it decreases fast with increasing temperature. When molecules of formaldehyde are exposed to a stream of high energy electrons we thus would expect they might be decomposed to an appreciable extent. That this is the case seems to be indicated by the data given in Table 7. The current through the reactor was exceptionally large indicating an unusually high degree of chemical activity but the yield of formaldehyde coming out was negligible. Washing the reactor with distilled water gave a colorless liquid that on evaporation gave a substantial amount of brownish residue.

The formation and subsequent decay of formaldehyde in a silent discharge might be somewhat analogous to the propagation of these processes in the case of the formation of hydrazine from ammonia. When the latter substance as a gas gasses through a silent discharge, the amount of hydrazine formed at a given flow rate passes through a well defined maximum as the amount of power dissipated is increased. The value for the maximum yield of hydrazine per KWH increases steadily with the ammonia flow rate, although the degree of ammonia conversion drops slowly. The power yield further increased with decreasing temperature, decreasing thickness of the dielectric and increasing length or active surface area of the reactor. Hydrazine decomposed in the discharge does not regenerate to ammonia and a certain amount of nitrogen is always liberated. In the case of formaldehyde it decomposes mainly to reform the monoxide under liberation of hydrogen.

Most studies that have appeared in the literature on the formation of formaldehyde from carbon monoxide and hydrogen in a silent discharge are quite limited in scope but a review of the data available should serve to illuminate the directions along which our own work might pro-

ceed. The appearance of formaldehyde as a reaction product was discovered more than sixty years ago by Losanitsch and Jovitschitsch (Ber. D. Chem. Ges. 30, 135, 1897). It was confirmed by Loeb (Z. Elektroch. 12, 282, 1906) and studied in further detail by Koenig and Weinig (Festschrift Techn. Hochschule zu Karlsruhe, 525, 1925) who used a glow discharge. They found that the formaldehyde produced is adsorbed on the walls of the reactor. The condensation product adhering to the walls could be removed only by intermittent or continuous washing with water. In this manner they succeeded in obtaining formaldehyde as the chief product of the action of the glow discharge with conversion yields up to 77%. The power yield was however only 2 grams per KWH consumed.

The most extensive study of the formation of formaldehyde in silent discharges has been carried out by Sahasrabudhey and his coworkers (Proc. Indian Sci. Congress, Chem. Sect. 1946, Abstr. 35, 49, 51 and 52; *ibid* 1947, Abstr. 9 to 11; Proc. Indian Academy of Science 27A, No. 5, 366-74, 1948; *ibid* 31A, 317-24, 1950; J. Indian Chem. Soc. 27, 361, 1950; *ibid* 28, 377, 1951). The set up finally adopted was fairly complicated. It consisted chiefly of a gas reservoir system and an arrangement for the circulation of the mixed gases combined with continuous stripping of the formaldehyde generated in gas bubbles. The all-glass reactor was of conventional, ozonizer type. Alternating current with a frequency of 500 c.p.s. was obtained using a 2 KVA motor generator. However, neither current nor power factor measurements appear to have been made, although excitation potentials of about 9.6 KV or higher were found necessary to get the reaction to take place. The best yields were obtained with an equimolar gas mixture but since the experiments were run over periods of six hours with a re-cycle rate of 8 liters per minute, the power yield is likely to have been low. For optimum conditions an amount of 16 grams of formaldehyde was indicated as produced per KWH dissipated. However, the power factor may have been neglected and since it would have a value of about 0.3 the actual maximum power yield may perhaps have been three times larger or approximately 50 grams of formaldehyde per KWH consumed. The net yield increased with the size of the reactor. Measurements of the yield over the temperature range of 25 to 80°C showed it to be practically constant. The reaction was found to be homogeneous and the yield increased with the



volume of the discharge space. The formation of  $\text{CO}_2$  and unsaturated hydrocarbons decreased with increasing discharge volume, indicating that they are formed as the result of heterogeneous reactions on the reactor walls.

Some experiments using separately excited hydrogen at a current of 500 milliamperes with 3000 volts applied have been carried out by M.F. Nagiev, R.M. Efendiev and F.G. Ismailzade (Doklady Akad. Nauk Azerbaidshan, 14, 347, 1958). The compounds obtained, as identified with a mass spectrograph, included besides formaldehyde,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Their results appear to be of sufficient interest to warrant further study. A reactor for the purpose is now available.

To complete our literature review it should be mentioned that three patents have been found for processes of the manufacture of formaldehyde from mixtures of carbon monoxide and hydrogen exposed to various types of electric discharges (1) S. Ruben, U.S. Patent No. 1,431,047, October 3, 1922; (2) Eloi Ricard, U.S. Patent No. 2,205,542, June 25, 1940; (3) P.X. Spillane, Australian Patent No. 111,151, July 29, 1940. The patent of E. Ricard indicates he obtained yields of 63 grams of formaldehyde per KWH consumed but it was all absorbed on charcoal as polyoxymethylene. The operating pressure was kept at one-tenth atmosphere with a gas mixture flow rate of 166 liters per minute for a reactor of 16" inner diameter. If it were possible to dissolve out the polyoxymethylene formed continuously, the method of E. Ricard might be suitable for use during travel in space. The main drawback to the apparatus required is its relatively large size and weight.

To summarize our review of data in the literature on the formation of formaldehyde, it is our impression that it should be chemically feasible to produce formaldehyde during extended travel in space at moderate power consumption, in quantities sufficient for conversion to carbohydrates for use as food.

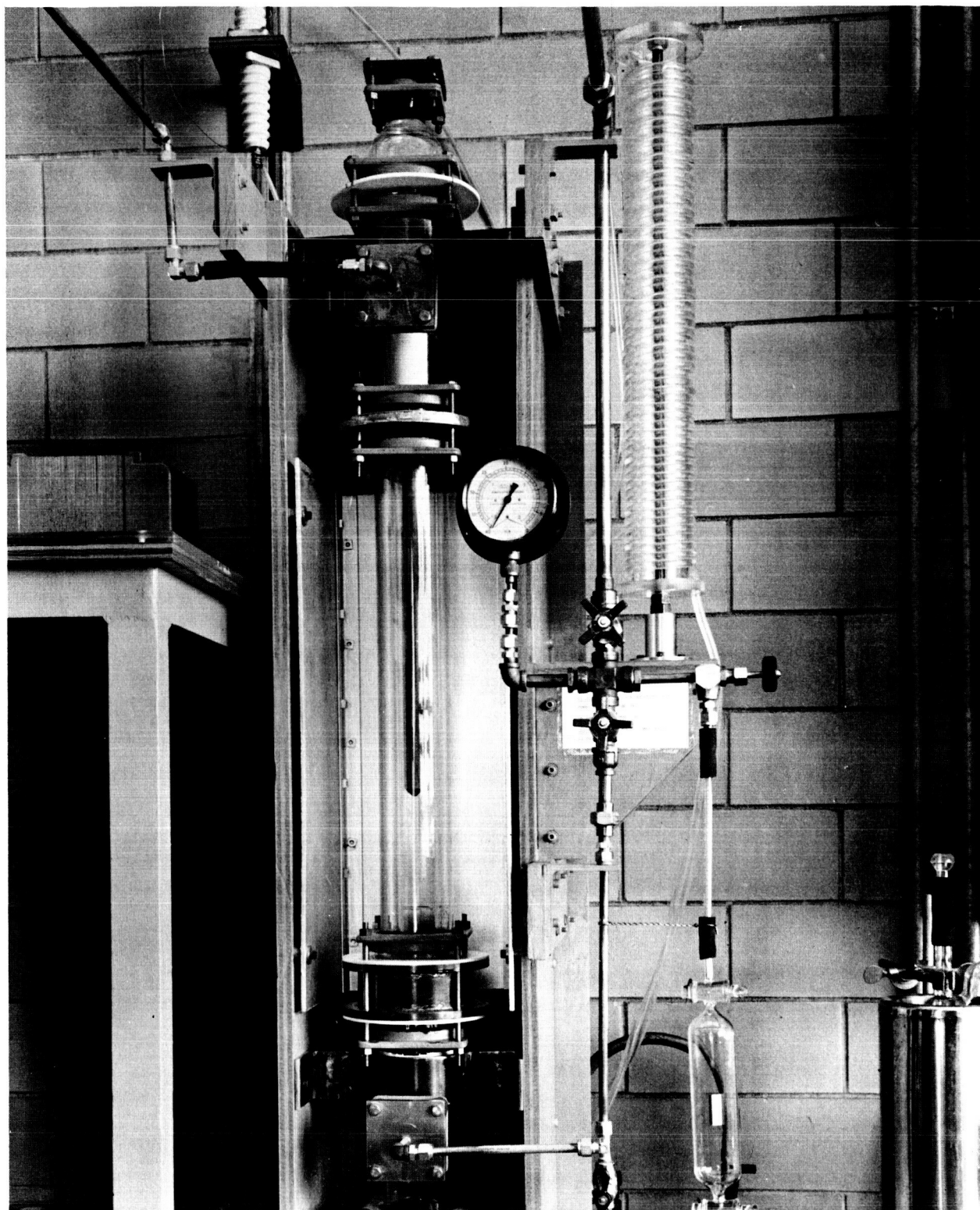


Figure 1. Glow Discharge Reactor

The coil on the right hand side provides a high resistance to the ground for the cooling water serving the HV electrode. The quenching unit below the HV carbon electrode is practically at ground potential and needs only a few feet of plastic tubing for its water cooling to provide adequate insulation.

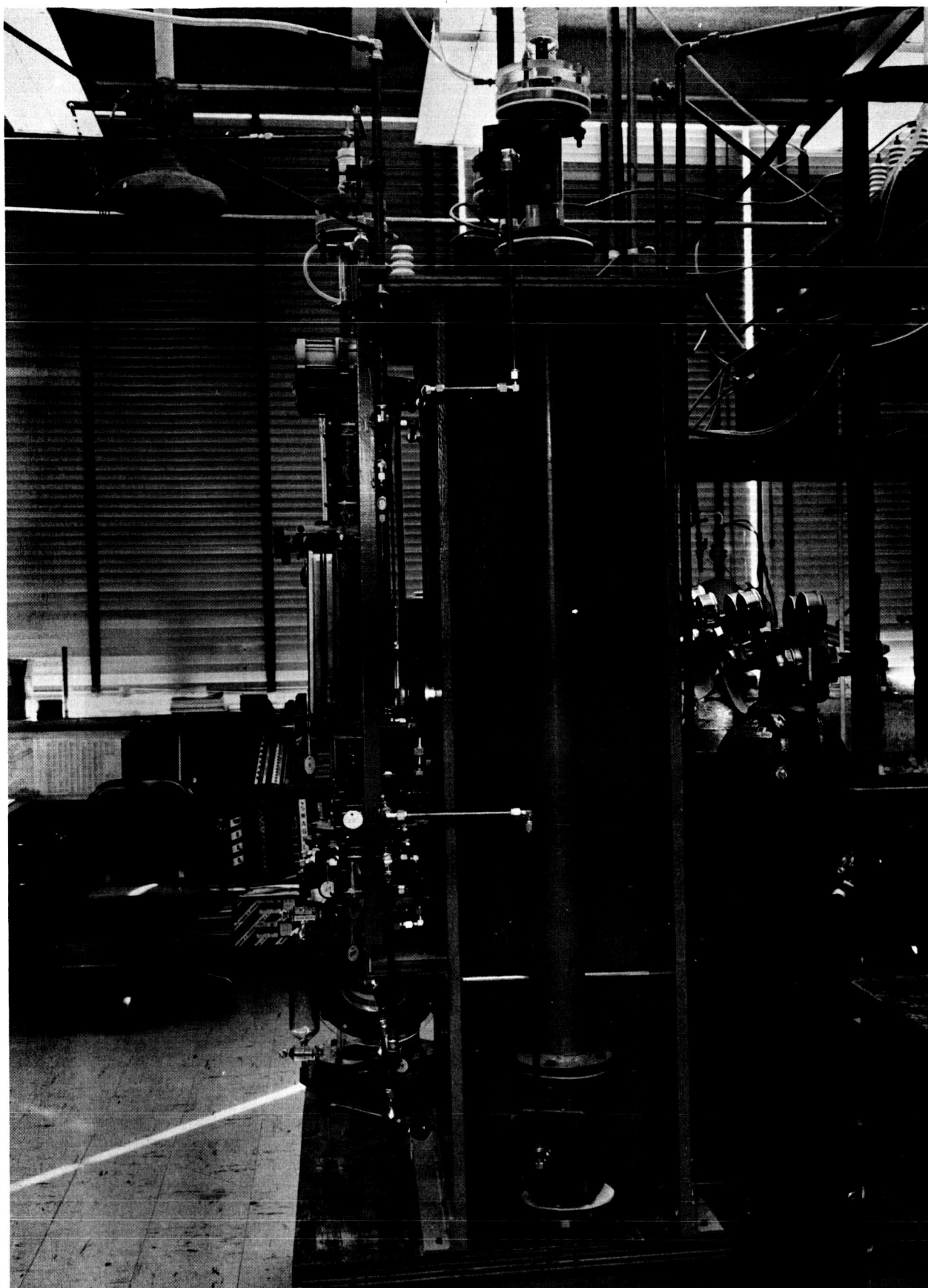


Figure 2. Silent Discharge Reactor

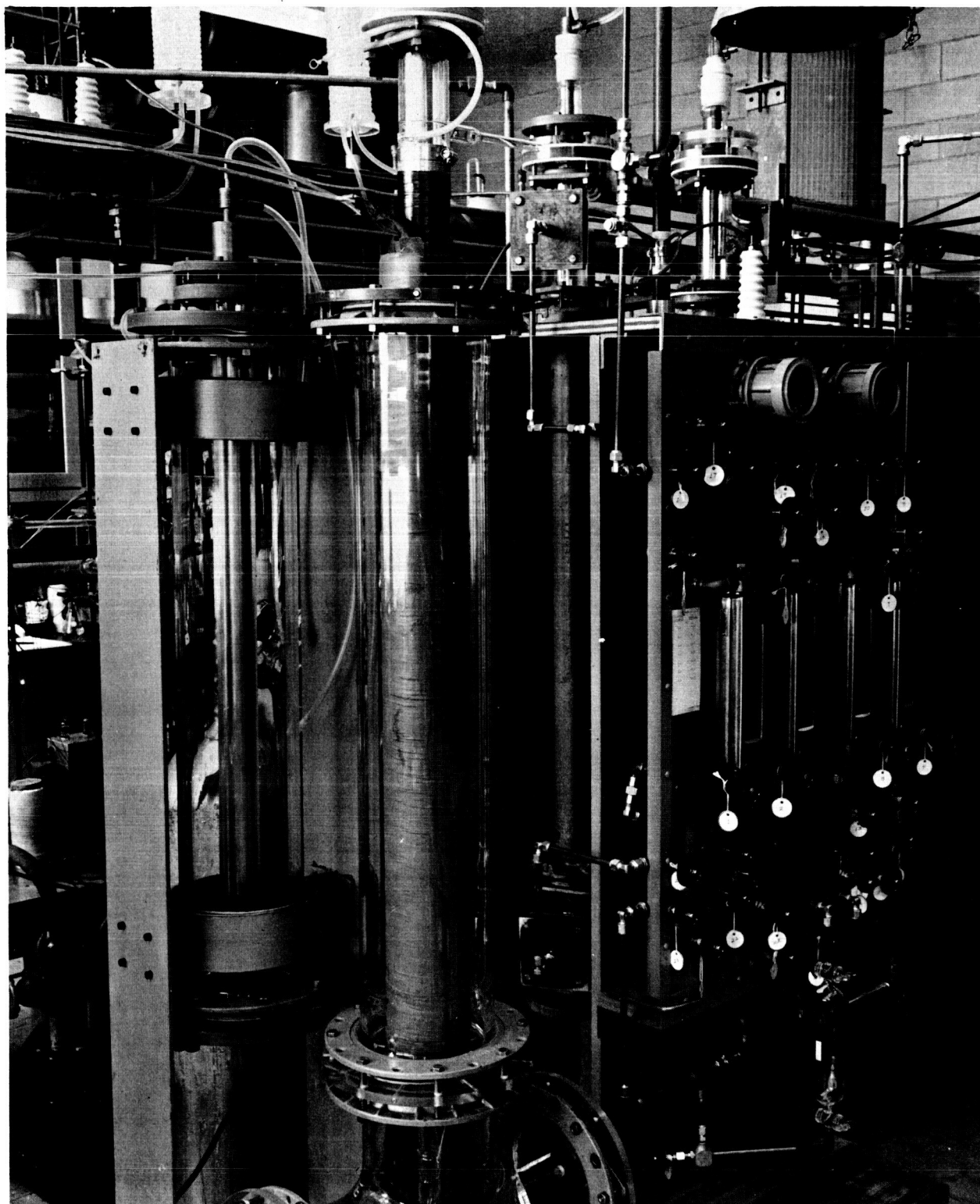


Figure 3. Various Silent Discharge Reactors

In the foreground center is seen the reactor with the solenoid coil, to the left the reactor with the water bath and center aluminum, water cooled electrode. To the right is seen a reactor similar to the one shown in Figure 2 but shorter and having a glass coated mantle tube.

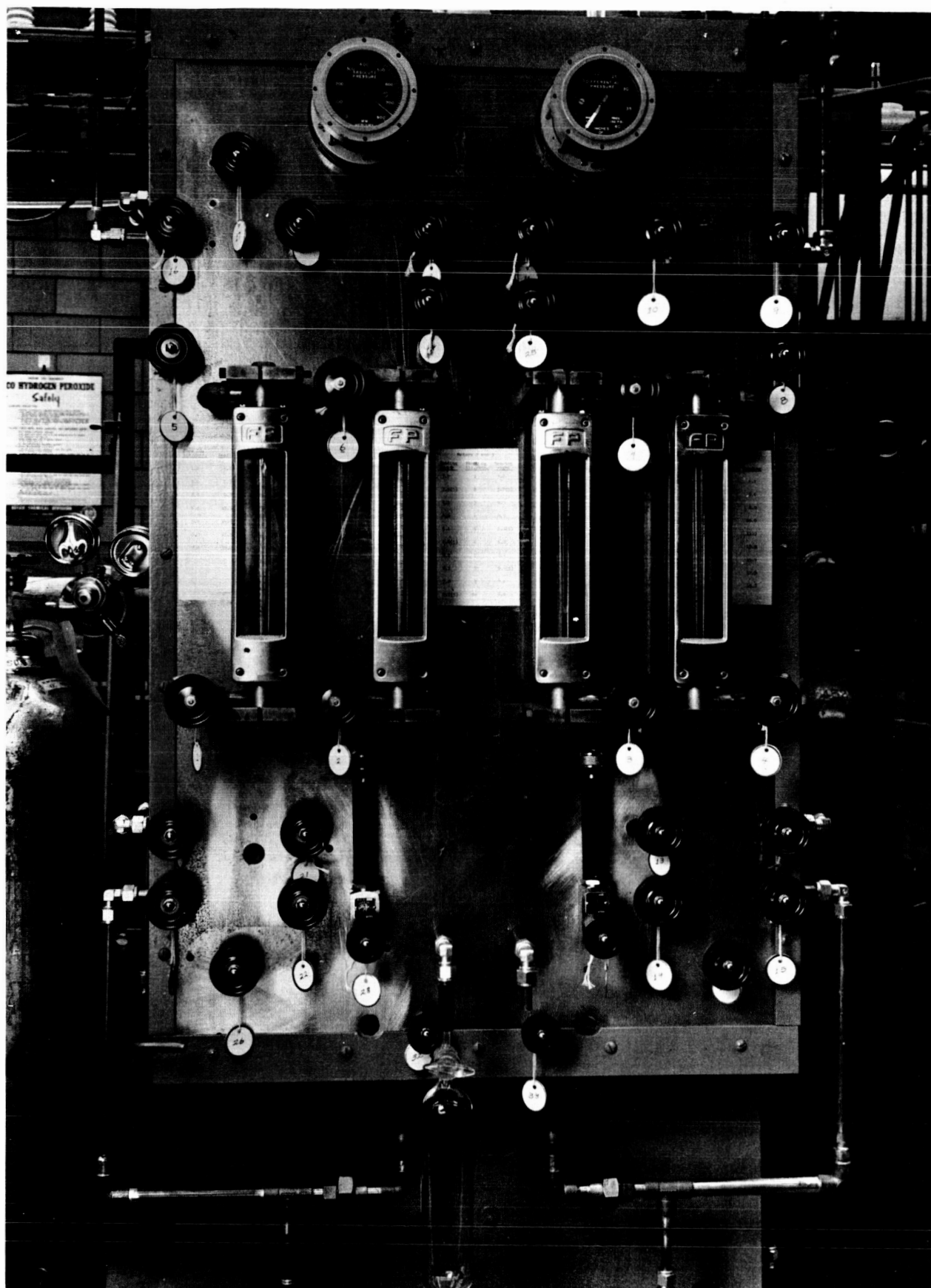


Figure 4. Flow Control Panel



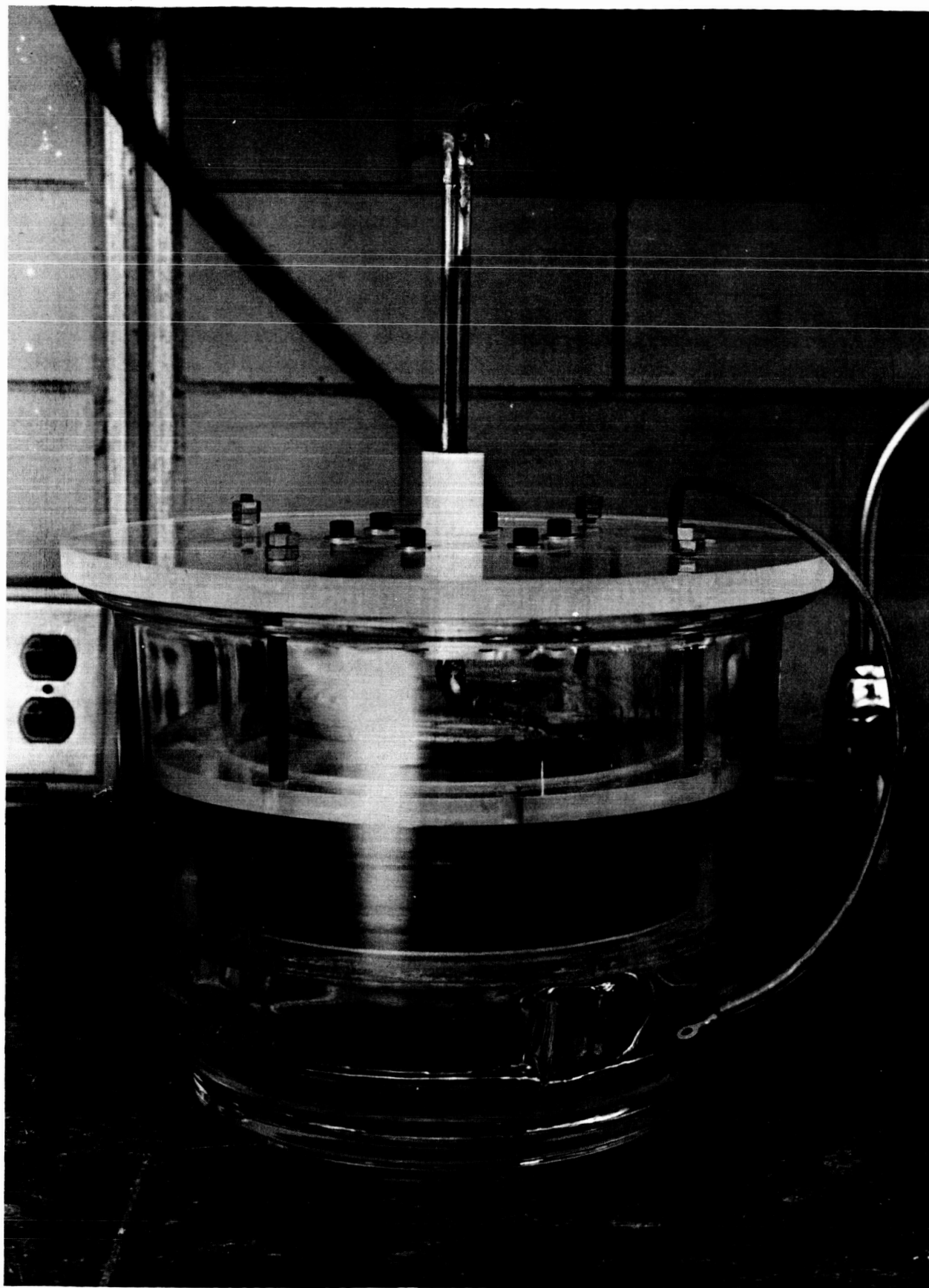


Figure 5. Silent Discharge Reactor for Operation  
with a Static Liquid Phase

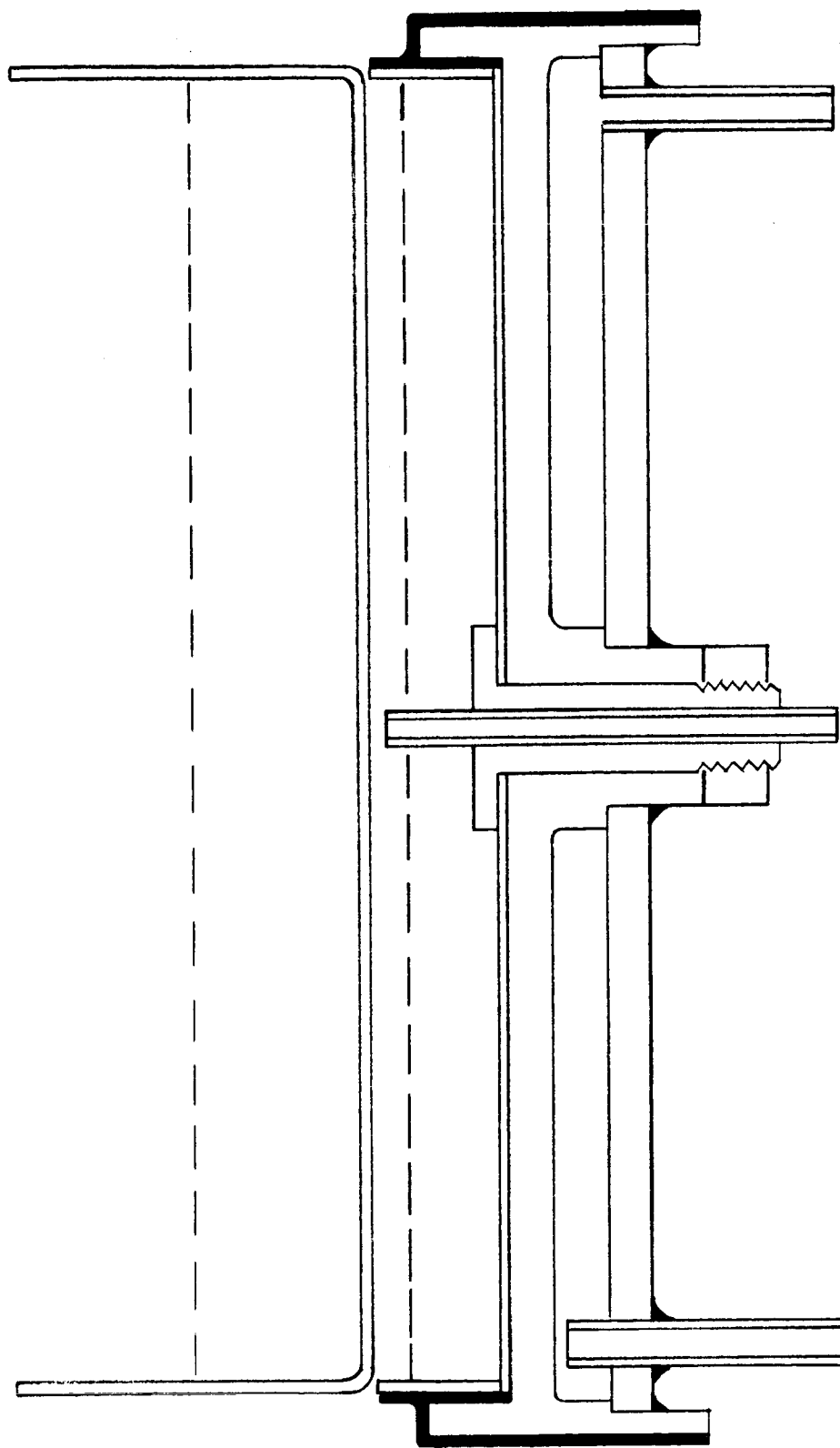


Figure 6. Diagram of Water Cooled Reactor for the Study of the Formation of  $\text{CH}_2\text{O}$  in a Silent Discharge from  $\text{CO}$  and  $\text{H}_2$  in the presence of a Liquid Phase

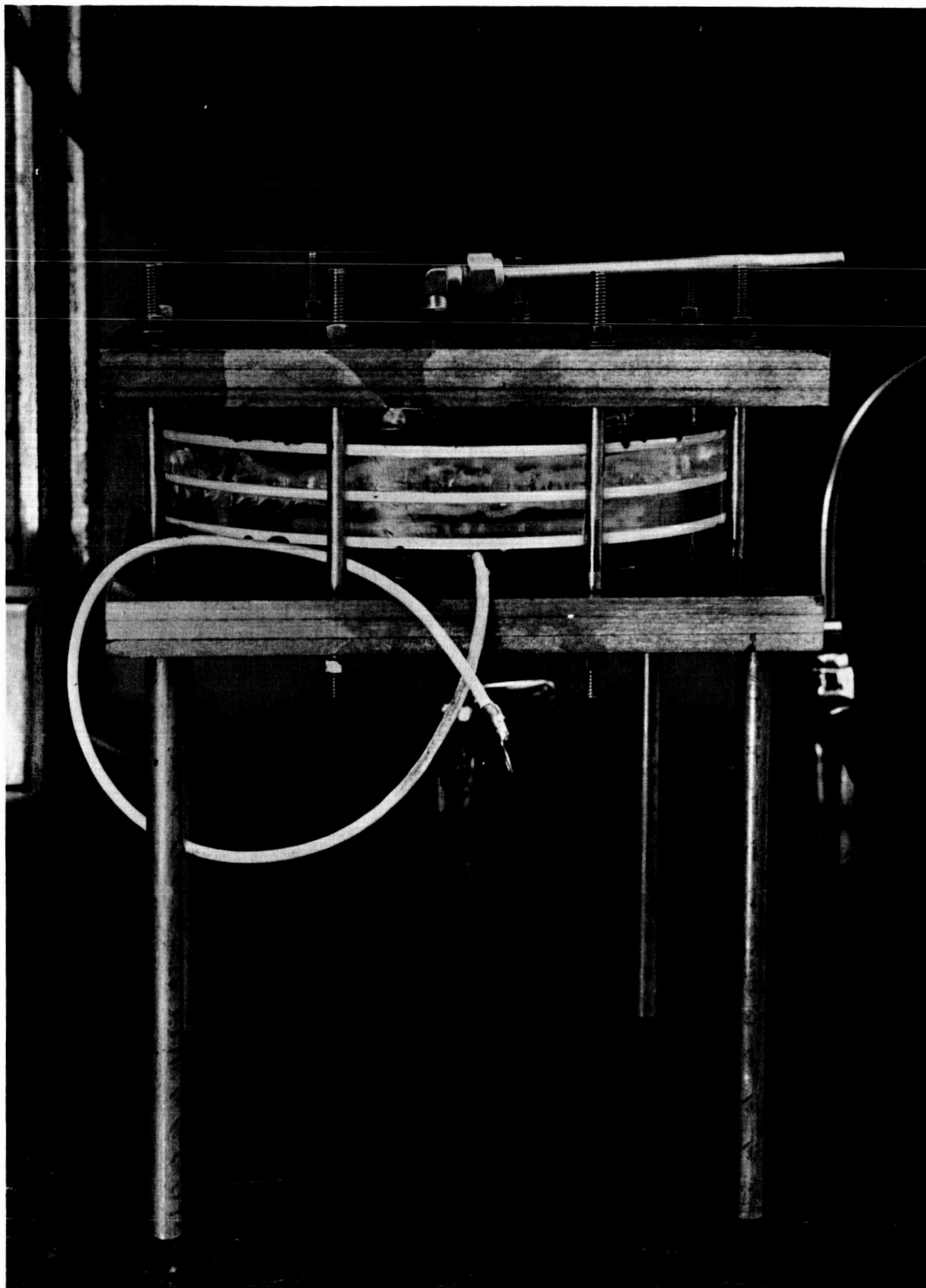


Figure 7. Corona Discharge Reactor



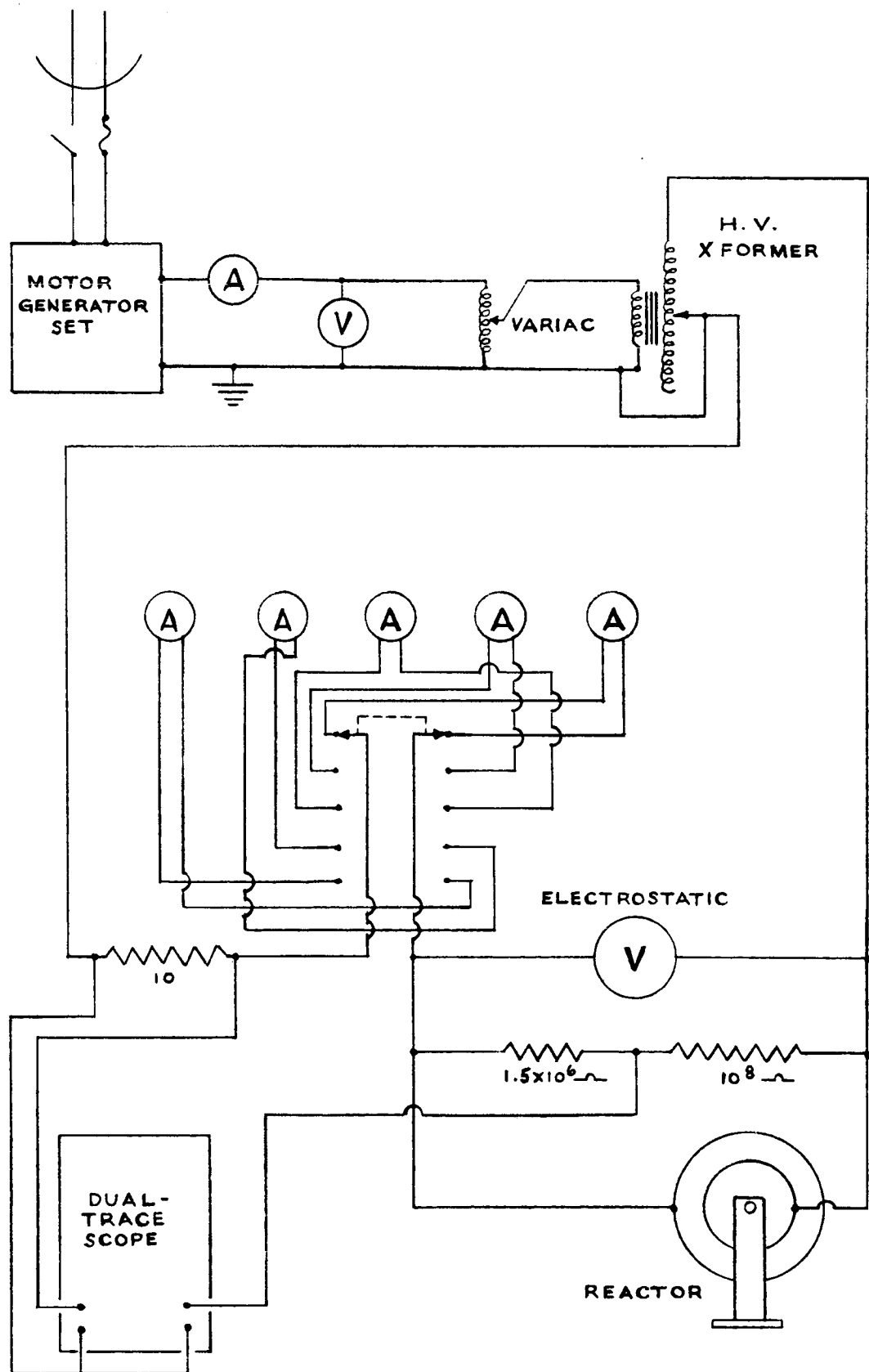


Figure 8. Diagram of Circuit for Silent Discharge Reactors Used

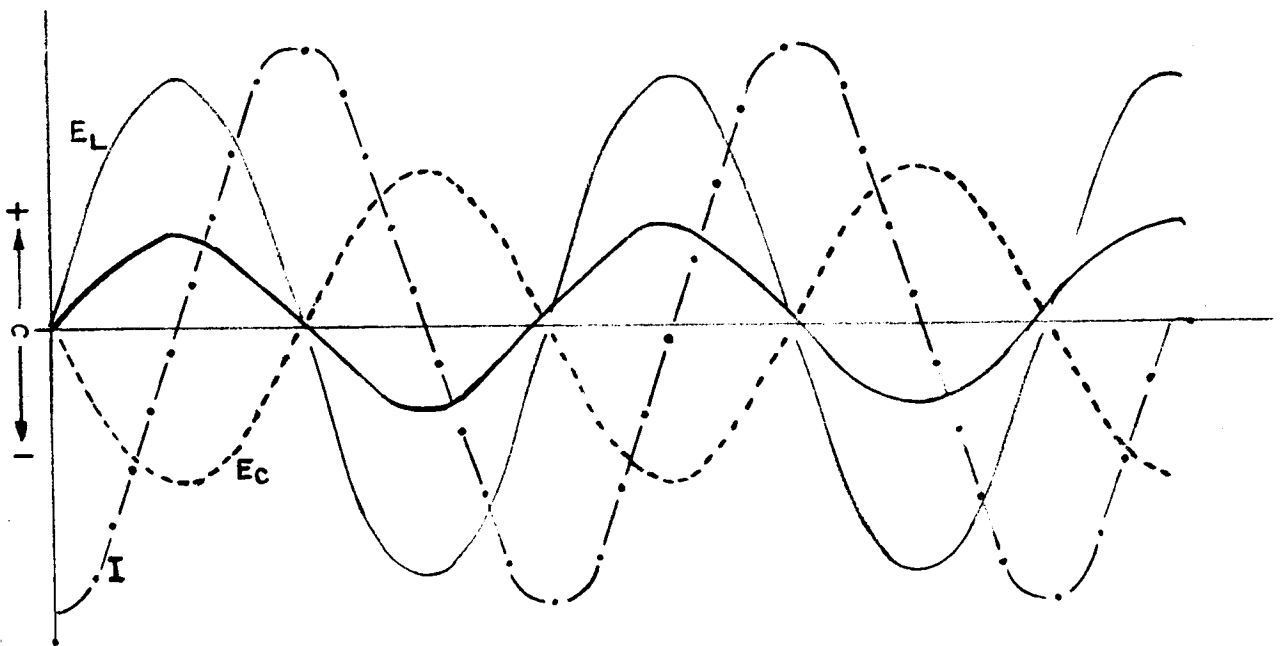
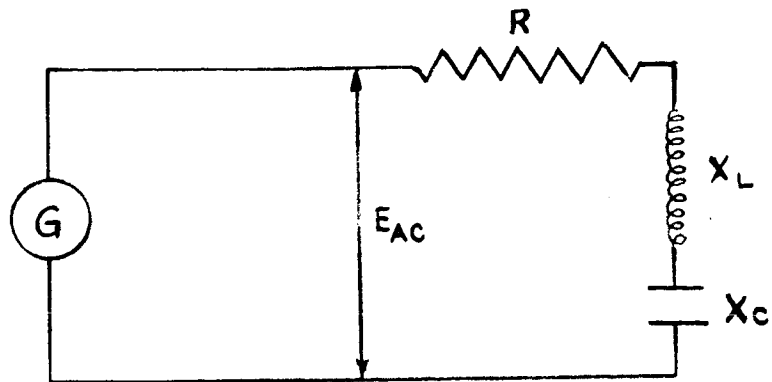


Figure 9. The heavy solid line  $E_L - E_C$  is the resultant voltage across the circuit. If  $E_L = E_C$  this voltage would be zero and the only voltage drop across the circuit would be the  $IR$  drop from ohmic resistance which would be in phase with the curve marked  $I$ . If  $R$  is too small this voltage would be insufficient to sustain the discharge.

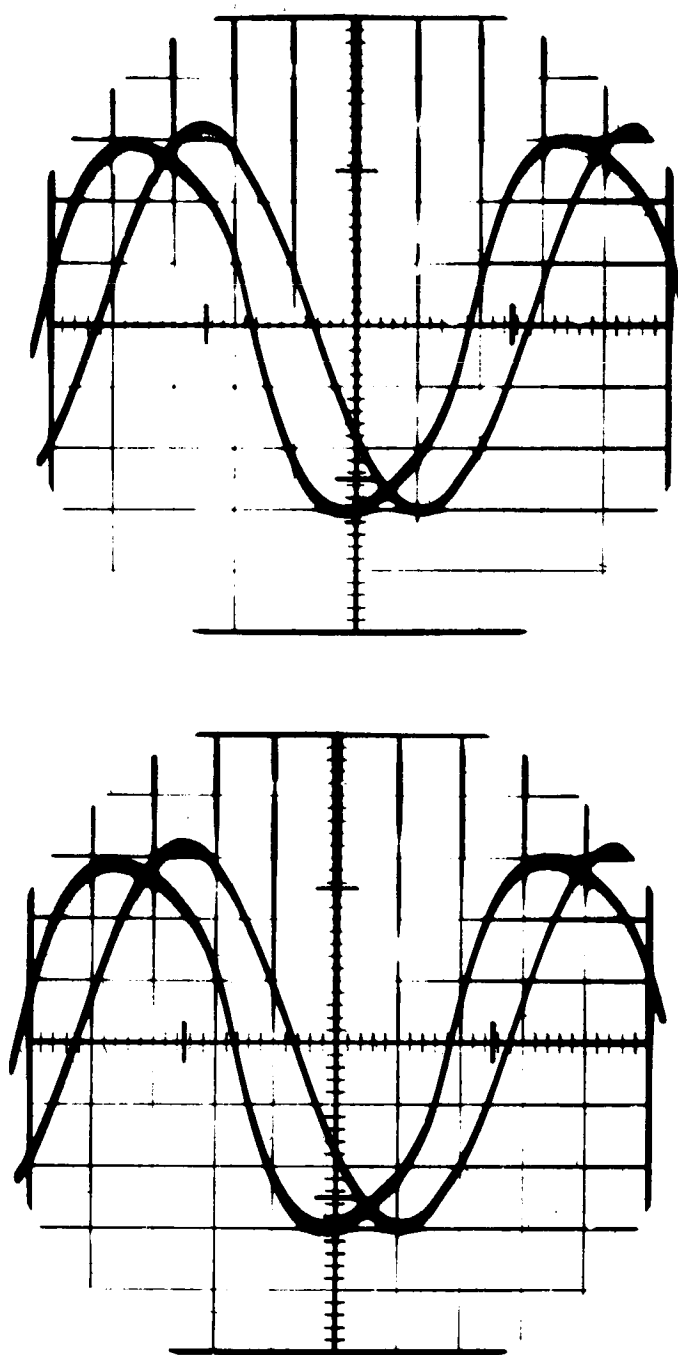


Figure 10. Current-Voltage Traces Obtained with Dumont Model 411 Oscilloscope for Determination of the Power Factor of the Discharge Current

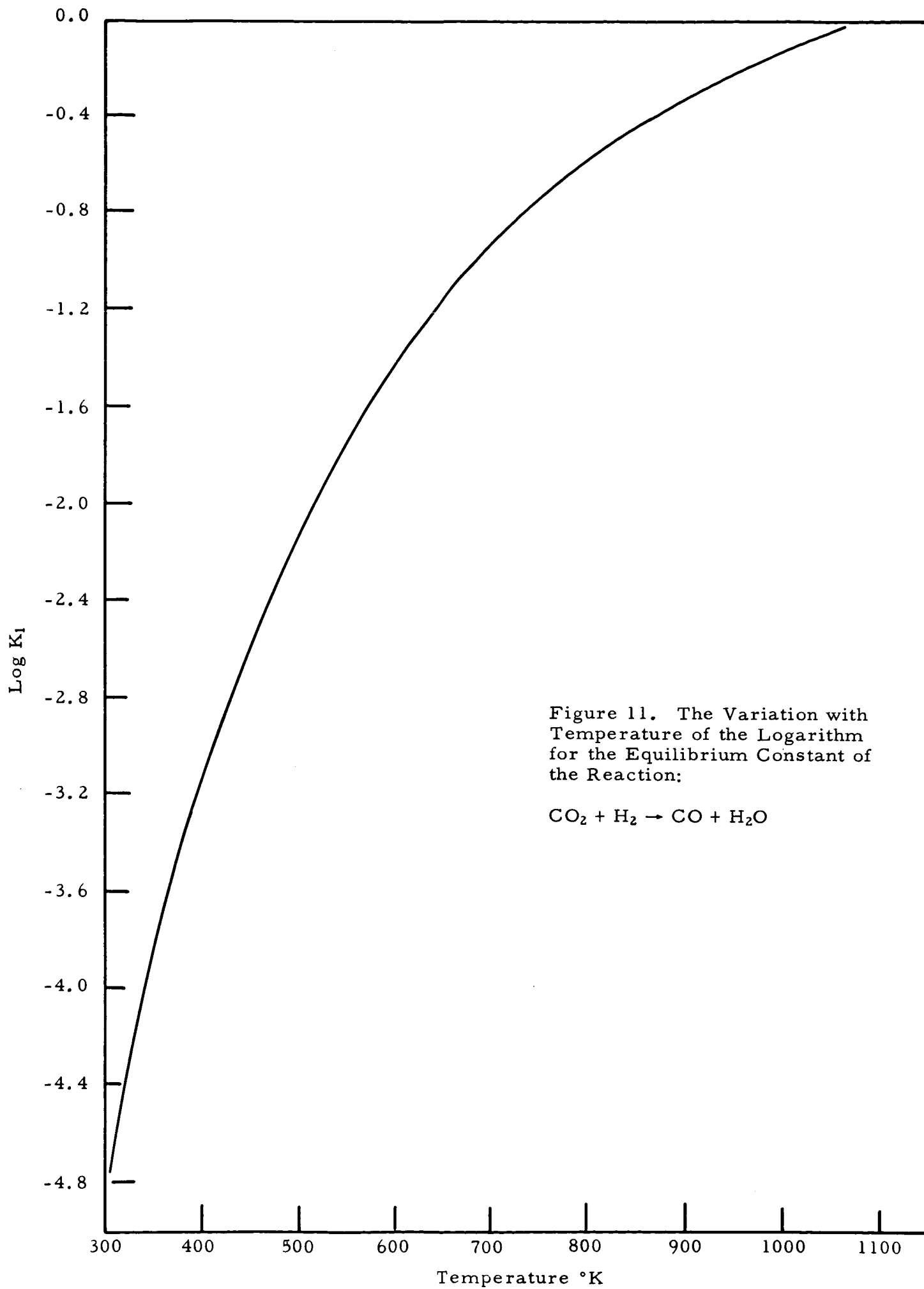
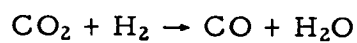


Figure 11. The Variation with Temperature of the Logarithm for the Equilibrium Constant of the Reaction:



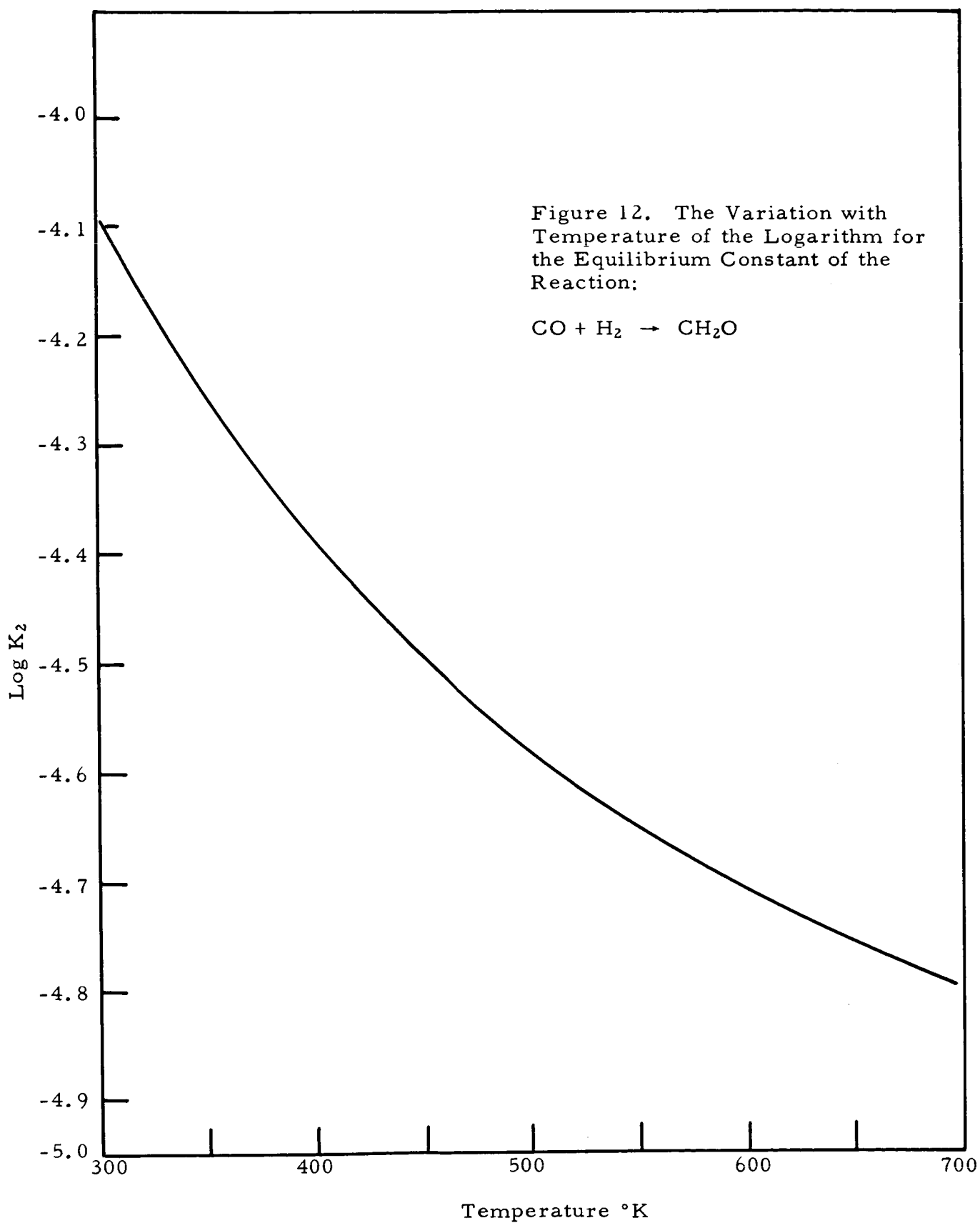


Table 1. The Conversion of Carbon Dioxide to the Monoxide in a DC Glow Discharge at an Electrode Separation of 20 cm.

A. Flow and Current Data

Sample Number	CO <sub>2</sub> Lit./min.	H <sub>2</sub> Lit./min.	P mm Hg	Ampere	KV	KW
2-26-1	3.0	3.0	17.2	0.84	2.0	1.68
2	4.0	4.0	22.5	0.76	2.4	1.82
3	5.0	5.0	26.0	0.66	2.8	1.85
4	4.0	6.0	24.5	0.74	2.6	1.92
5	4.0	8.0	27.0	0.70	2.8	1.96
6	4.0	10.0	29.0	0.69	2.9	2.00
2-27-1	4.0	4.0	26	0.78	2.5	1.95
2	4.0	6.0	26	0.74	2.7	2.00
3	4.0	8.0	27	0.66	3.1	2.05
4	4.0	10.0	30	0.66	3.1	2.05
5	3.0	12.0	28	0.74	2.8	2.07
6	4.0	3.0	26	0.72	2.7	1.94
7	4.0	2.0	26	0.77	2.4	1.85
8	4.0	2.0	26	0.76	2.4	1.82
9	4.0	4.0	26	0.73	2.6	1.90
10	4.0	4.0	26	0.72	2.6	1.87

B. Analytical Data

Sample Number	H <sub>2</sub> Vol. %	H <sub>2</sub> O Vol. %	CO Vol. %	CO <sub>2</sub> Vol. %	Ratio CO/(CO + CO <sub>2</sub> )
2-26-1	15.6	5.1	44	35.3	0.56
2	18.7	7.5	42	31.8	0.57
3	18.4	7.3	38	36.3	0.51
4	39.6	6.1	37	17.3	0.68
5	44.3	5.4	35	15.3	0.70
6	54.3	4.8	29	11.9	0.71
2-27-1	14.4	5.8	44.3	35.5	0.56
2	29.6	7.5	42.9	19.9	0.68
3	44.5	5.5	36.8	13.2	0.74
4	55.9	3.7	29.2	11.2	0.72
5	61.2	4.5	27.3	7.0	0.80
6	7.7	5.8	39.8	46.7	0.46
7	4.1	4.9	30.6	60.4	0.42
8	4.0	6.5	30.2	59.2	0.34
9	16.1	6.1	43.7	34.1	0.56
10	18.0	4.4	43.6	34.0	0.56

Maximum yield of carbon monoxide about 110 gr./KWH. All analytical data given in this report supplied by the Analytical Department

Table 2. The Conversion of Carbon Dioxide to the Monoxide in a DC Glow Discharge at an Electrode Separation of 15 cm.

A. Flow and Current Data

<u>Sample Number</u>	<u>CO<sub>2</sub> lit./min.</u>	<u>H<sub>2</sub> lit./min.</u>	<u>P mm Hg</u>	<u>Ampere</u>	<u>KV</u>	<u>KW</u>
3-2-1	4.0	4.0	35	0.74	1.8	1.33
2	4.0	6.0	35	0.72	2.0	1.44
3	4.0	8.0	35	0.70	2.0	1.40
4	4.0	10.0	35	0.69	2.1	1.45
5	4.0	12.0	35	0.67	2.2	1.47
6	4.0	14.0	35	0.65	2.3	1.49
7	4.0	16.0	35	0.64	2.4	1.53
8	4.0	18.0	35	0.62	2.5	1.55
9	4.0	20.0	36	0.61	2.5	1.52
10	3.0	20.0	35	0.64	2.4	1.54

B. Analytical Data

<u>Sample Number</u>	<u>H<sub>2</sub> vol. %</u>	<u>H<sub>2</sub>O vol. %</u>	<u>CO vol. %</u>	<u>CO<sub>2</sub> vol. %</u>	<u>Ratio CO/(CO + CO<sub>2</sub>)</u>
3-2-1	18.7	3.8	32.1	45.4	0.41
2	25.5	5.2	32.7	36.6	0.49
3	55.7	3.4	11.3	29.6	0.28
4	56.2	2.6	19.7	21.5	0.48
5	60.7	2.4	16.6	20.2	0.45
6	67.0	2.1	13.3	17.6	0.43
7	62.8	2.3	9.3	13.2	0.41
8	74.3	1.3	9.4	15.0	0.39
9	73.3	1.8	9.1	15.8	0.37
10	81.4	0.9	7.1	10.6	0.40

The narrow range for the degree of conversion is surprising in view of the large changes in the relative amounts of hydrogen present.

Table 3. Data Obtained for Some Runs with CO - H<sub>2</sub> Mixtures Exposed to a DC Glow Discharge at an Electrode Separation of 15 cm.

A. Flow and Current Data

<u>Sample Number</u>	<u>CO</u> <u>lit./min.</u>	<u>H<sub>2</sub></u> <u>lit./min.</u>	<u>P</u> <u>mm Hg</u>	<u>Amperes</u>	<u>KV</u>	<u>KW</u>
3-12-11	4.0	6.0	15	0.80	1.2	0.96
12	4.0	6.0	20	0.80	1.3	1.04
13	4.0	6.0	25	0.80	1.3	1.04
14	4.0	6.0	30	0.80	1.4	1.12
15	4.0	6.0	35	0.80	1.5	1.20
16	4.0	6.0	40	0.80	1.6	1.28
3-13-11	4.0	6.0	30	0.80	1.5	1.20
12	4.0	8.0	30	0.80	1.6	1.28
13	4.0	10.0	30	0.80	1.7	1.36
14	4.0	12.0	30	0.80	1.8	1.44
15	4.0	14.0	30	0.80	1.9	1.52
16	4.0	16.0	30	0.80	2.0	1.60

B. Analytical Data

<u>Sample Number</u>	<u>H<sub>2</sub></u> <u>vol. %</u>	<u>H<sub>2</sub>O</u> <u>vol. %</u>	<u>CO</u> <u>vol. %</u>	<u>CO<sub>2</sub></u> <u>vol. %</u>	<u>Ratio (H<sub>2</sub>)/(CO)</u>	
					<u>Flow</u>	<u>Analytical</u>
3-12-11	87.4	0.2	12.2	0.1	1.50	7.2
12	87.2	0.2	12.5	0.04	1.50	7.0
13	84.7	0.2	13.4	1.6	1.50	6.3
14	81.7	0.4	16.7	1.1	1.50	4.9
15	-	-	-	-	1.50	-
16	86.6	0.1	13.2	0.01	1.50	6.6
3-13-11	57.1	0.1	42.7	0.02	1.50	1.3
12	61.8	0.2	37.7	0.02	2.00	1.6
13	63.9	0.3	35.8	0.03	2.50	1.8
14	73.9	0.1	26.0	0.00	3.00	2.8
15	74.8	0.1	23.8	0.01	3.50	3.1
16	-	-	-	-	4.00	-

The analytical data for samples 3-12-11 to 16 seem to be somewhat strange and they are not in line with those of samples 3-13-11 to 15. Be this as it may, the CO<sub>2</sub> content of all the samples appears to be small.



Table 4. The Conversion of Carbon Dioxide to the Monoxide in a Silent Discharge at Atmospheric Pressure and Ordinary Temperatures. Reactor Length 36 inches, Annular diameter 3/16 inch.

A. Flow and Current Data

<u>Sample Number</u>	<u>CO<sub>2</sub> lit./min.</u>	<u>H<sub>2</sub> lit./min.</u>	<u>Milliamp.</u>	<u>KV</u>
2-28-1	2.0	2.0	78	7.7
2	3.0	3.0	78	7.7
3	4.0	4.0	79	7.6
4	5.0	5.0	79	7.6
5	6.0	6.0	78	7.8
6	7.0	7.0	78	7.8
7	4.0	8.0	76	7.3
8	4.0	10.0	78	7.4
9	6.0	4.0	80	8.0
10	6.0	3.0	80	8.0

B. Analytical Data

<u>Sample Number</u>	<u>H<sub>2</sub> vol. %</u>	<u>H<sub>2</sub>O vol. %</u>	<u>CO vol. %</u>	<u>CO<sub>2</sub> vol. %</u>	<u>Ratio CO/(CO + CO<sub>2</sub>)</u>
2-28-1	40.1	0.1	1.0	58.8	0.017
2	36.6	0.8	1.3	61.3	0.021
3	37.9	0.1	0.7	61.3	0.014
4	30.0	-	0.6	69.4	0.008
5	36.8	-	0.6	62.6	0.009
6	42.2	-	0.5	57.3	0.009
7	54.6	0.1	0.5	44.8	0.012
8	51.6	0.2	0.5	47.7	0.011
9	22.6	0.1	1.0	76.3	0.013
10	26.2	-	0.8	73.0	0.011

Assuming power factor of 0.3 average yield of CO = 21 grams/KWH

Table 5. The Conversion of Carbon Dioxide to the Monoxide in a Silent Discharge at Atmospheric Pressure and Ordinary Temperatures. Reactor Length 50 Inches, Annular Diameter 3/16 Inch.

A. Flow and Current Data

<u>Sample Number</u>	<u>CO<sub>2</sub> lit./min.</u>	<u>H<sub>2</sub> lit./min.</u>	<u>Milliamp.</u>	<u>KV</u>
3-9-1	2.0	2.0	83	7.9
2	3.0	3.0	83	7.8
3	4.0	4.0	84	7.8
4	5.0	5.0	84	7.8
5	4.0	6.0	84	7.6
6	4.0	7.0	84	7.5
7	4.0	8.0	83	7.4
8	4.0	9.0	83	7.3
9	4.0	10.0	82	7.2
10	3.0	3.0	84	7.8

B. Analytical Data

<u>Sample Number</u>	<u>H<sub>2</sub> vol. %</u>	<u>H<sub>2</sub>O vol. %</u>	<u>CO vol. %</u>	<u>CO<sub>2</sub> vol. %</u>	<u>Ratio CO/(CO + CO<sub>2</sub>)</u>
3-9-1	33.4	0.1	1.0	65.5	0.015
2	46.2	0.6	0.6	53.2	0.014
3	37.6	-	0.5	61.9	0.008
4	47.0	-	0.5	52.5	0.009
5	55.8	-	0.4	43.8	0.010
6	60.0	-	0.4	39.6	0.010
7	57.7	-	0.3	42.0	0.007
8	65.2	-	0.4	34.4	0.012
9	64.9	-	0.4	34.7	0.011
10	35.0	-	0.8	64.2	0.012

In the case of both reactors the degree of conversion of CO<sub>2</sub> is practically the same and independent of the composition of the gas mixture, 0.012 for the shorter and 0.011 for the longer one.

Table 6.     The Conversion of Carbon Dioxide to the Monoxide in a Silent Discharge at Atmospheric Pressure and a Temperature of 94°C.

A. Flow and Current Data at an Annular Diameter of 3/16 Inch

<u>Sample Number</u>	<u>CO<sub>2</sub> lit./min.</u>	<u>H<sub>2</sub> lit./min.</u>	<u>Milliamp.</u>	<u>KV</u>
3-15-1	2.0	2.0	90	6.7
2	3.0	3.0	90	6.7
3	4.0	4.0	90	6.7
4	5.0	5.0	90	6.7
5	6.0	6.0	90	6.7
6	7.0	7.0	90	6.7

B. Flow and Current Data at an Annular Diameter of 9/16 Inch

3-16-1	2.0	2.0	90	13.1
2	3.0	3.0	90	12.9
3	4.0	4.0	90	12.8
4	4.0	4.0	90	12.8
5	5.0	5.0	90	12.8
6	5.0	5.0	90	12.8

Length of Reactor 50 inches. A slight trickle of water was allowed to flow through the cooling unit for the center glass tube of the reactor.

Table 6. (Continued) Analytical Data

C. For Runs Using Reactor with Annular Diameter of 3/16 Inch

<u>Sample Number</u>	<u>H<sub>2</sub> vol. %</u>	<u>H<sub>2</sub>O vol. %</u>	<u>CO vol. %</u>	<u>CO<sub>2</sub> vol. %</u>	<u>Ratio CO/(CO + CO<sub>2</sub>)</u>
3-15-1	49.3	0.22	1.4	49.1	0.028
2	40.0	0.05	0.6	59.4	0.010
3	32.9	0.10	0.9	66.1	0.011
4	43.0	0.03	0.6	56.4	0.011
5	45.2	-	0.6	54.2	0.011
6	35.1	-	0.5	64.4	0.008
Average					0.011

D. For Runs Using Reactor with Annular Diameter of 9/16 Inch

3-16-1	48.5	0.1	1.4	50.0	0.027
2	42.9	0.2	1.2	55.7	0.021
3	44.8	0.2	0.6	54.4	0.011
4	31.7	0.2	0.8	67.3	0.012
5	43.6	0.2	0.6	55.6	0.011
6	40.0	0.2	0.6	59.2	0.010
Average					0.015

A slight increase in the degree of conversion of CO<sub>2</sub> to CO may perhaps take place with increasing annular diameter.

Table 7. Data for Various Runs with CO - H<sub>2</sub> Mixtures in a Silent Discharge at Atmospheric Pressure and Ordinary Temperatures. Reactor Length 50 Inches, Annular Diameter 3/16 Inch.

A. Flow and Current Data

<u>Sample Number</u>	<u>CO</u> <u>lit./min.</u>	<u>H<sub>2</sub></u> <u>lit./min.</u>	<u>Milliamp.</u>	<u>KV</u>
3-8-1	1.0	1.0	225	8.4
2	2.0	2.0	225	8.4
3	3.0	3.0	205	8.4
4	4.0	4.0	185	8.4
5	5.0	5.0	180	8.4
6	6.0	6.0	175	8.4
7	7.0	7.0	170	8.4
8	8.0	8.0	170	8.4
9	9.0	9.0	165	8.4
10	9.0	10.0	160	8.2

B. Analytical Data

<u>Sample Number</u>	<u>H<sub>2</sub></u> <u>vol. %</u>	<u>H<sub>2</sub>O</u> <u>vol. %</u>	<u>CO</u> <u>vol. %</u>	<u>CO<sub>2</sub></u> <u>vol. %</u>	<u>Ratio (H<sub>2</sub>)/(CO)</u>	
					<u>Flow</u>	<u>Analytical</u>
3-8-1	45.2	0.7	53.7	0.2	1.00	0.84
2	39.5	0.5	59.7	0.2	1.00	0.66
3	41.8	0.5	57.6	0.1	1.00	0.72
4	45.0	0.3	54.6	0.1	1.00	0.82
5	44.9	0.3	54.7	0.1	1.00	0.82
6	47.3	0.2	52.4	0.1	1.00	0.90
7	41.0	0.2	58.7	0.1	1.00	0.70
8	45.8	0.1	54.0	0.1	1.00	0.85
9	41.5	0.0	58.5	0.04	1.00	0.71
10	51.5	0.0	48.4	0.1	1.11	1.07

The violent fluctuations in the analytical values for the ratio (CO)/(H<sub>2</sub>) are difficult to understand. During any one of the discharge experiments the gas flow meters held steady at the readings required without visible changes. The leak rate of the reactor when fully exhausted was less than 0.1 mm Hg per minute. The air content of all the samples was recorded as 0.0%, formaldehyde content 0.0%.

## CHAPTER 2. CONVERSION OF CARBON DIOXIDE TO CARBON MONOXIDE AND SUBSEQUENT FORMALDEHYDE GENERATION

### Introduction

Further study of the reaction between carbon dioxide and hydrogen in a glow discharge has shown that conversions to carbon monoxide of up to 90% per pass may be achieved readily although at the cost of an appreciably higher power consumption of about 11-12 KWH per pound generated. The total weight of the electrodes and the reactor employed was less than 3 pounds. Gas flows providing conversion of sufficient quantities of carbon dioxide to supply a crew of five with formose sugar would be feasible using a single reactor of about the same size as the one employed so far.

Some preliminary data were obtained for the generation of formaldehyde from mixtures of pure carbon dioxide and hydrogen in silent discharges. The rate of formation in a tubular reactor accelerates strongly with increasing current, provided however, that adequate amounts of water are injected to absorb rapidly the formaldehyde generated. At a given current the presence of a magnetic field increased the yield of formaldehyde.

### I. The Conversion of Carbon Dioxide to Monoxide in a Glow Discharge

The data given in Chapter 1 with respect to the reaction between carbon dioxide and hydrogen in a glow discharge under formation of carbon monoxide seemed to indicate that a degree of conversion of 90% should be attainable. A few more measurements were first made after insertion in the reactor previously used of a still narrower center Vycor tube, thereby decreasing the inner diameter of the reactor to 2.66 cm. With the discharge on, the lower part of this tube gave off a fairly intense light. It was later found to have been strongly corroded, presumably due to the formation of silane.

As shown by the data summarized in Tables 1 to 4, the degree of conversion of carbon dioxide to monoxide appears to be substantially independent, within the ranges employed, of the composition, flow rates and pressure of

the gas stream. Exchange of the upper, water-cooled copper electrode with one of graphite lowered the degree of conversion sharply. The data in Table 2 are considered more reliable than Table 1. In neither case did the small Vycor tube improve conversion. Removal of the center Vycor tube and retaining the carbon cathode raised the yield of carbon monoxide per KWH approximately sevenfold, but the yield per KWH still remained substantially constant with varying pressure and composition of the original gas mixture. A carbon anode could not be used because it would disintegrate in a glow discharge.

At this point the reactor used so far was substituted with a water-cooled, all glass reactor having water-cooled electrodes. This new reactor is shown in Figure 1 with one of the copper electrodes exchanged with a non-cooled one made of graphite. The average inner diameter of the reactor tube proper was 0.875 inch. The shell was made of 2-inch Pyrex pipe and it should be able to withstand relatively severe shaking or mechanical shock. The total weight of the reactor with two copper electrodes was 1633 grams, with one graphite and one copper electrode 1344 grams.

The data obtained with the new reactor using copper electrodes are given in Table 5. The degree of conversion appears independent of pressure. However, when the copper cathode was replaced with carbon the data shown in Table 6 indicates the degree of conversion varies directly with pressure. Using the data of Table 6, the effect in the feed gas of hydrogen to carbon dioxide on the degree of conversion of carbon dioxide is shown in Table 7 and Figure 2. The carbon dioxide conversion appears to go through a maximum of 90% at a hydrogen to carbon dioxide ratio of about 3. By employing a somewhat larger distance between the electrodes it may be possible to obtain degrees of conversion in excess of 90%, but the power yield would be lowered. An increase in operating pressure would decrease the size and weight of the vacuum equipment required, but the pressure increase raises the voltage necessary to sustain the discharge, the size of the power supply and the power dissipation in the discharge. The increased power dissipation might be partly compensated by operating at a lower degree of conversion of the carbon dioxide.

To summarize the work on the conversion of carbon dioxide to carbon monoxide, it has been proven possible by use of a small, lightweight reactor with a maximum voltage of 4KV, to attain a 90% conversion of

carbon dioxide at a hydrogen to carbon dioxide volume ratio of about 3:1. The power yield at maximum conversion was about 38 grams of carbon monoxide per KWH. However, at a conversion of only 80% and using higher gas flow rates, yields per KWH several times higher are readily attainable. An appreciable fraction of the energy dissipated in the discharge may be recovered as heat and used for other purposes like distillation of water, concentration of sugar solutions, etc. With the necessary power available the first chemical step in our food to food process for a closed circuit respiratory system is thus feasible and able to provide fully adequate quantities of raw material for the next step, the synthesis of formaldehyde.

## II. Preliminary Data Obtained for the Reaction Between CO and Hydrogen In Silent Discharges

As indicated in the first chapter, the use of a 50" long silent discharge reactor with a dry gas mixture gave no formaldehyde. Introducing water as a fine spray in a circle around the top end of the glass center tube gave only very small amounts as shown by the titration data plotted in Figure 3, which represents the amount of formaldehyde generated after various lengths of time. The reactor shown in Figures 5 and 6 of the previous chapter gave appreciably better power yields, but the reproducibility was poor and the operation of the reactor tedious.

To get more uniform results a reactor was built with considerably larger liquid surface area and to maintain the distance between the surface of the liquid and the glass discharge plate within narrow limits. By continuous circulation of the liquid and measurement of the increase of the formaldehyde concentration the overall kinetics of formaldehyde formation should be measurable as function of the power consumed.

The design of this reactor is illustrated by the assembly drawing shown in Figure 4 and the photographs in Figures 5 and 6. Pure water is circulated in at a measured rate over the thin edge of the micarta ring into the bottom section from where it drains into a stand pipe connected with the



intake of the circulating pump. The edge of the plate glass diaphragm suspended above the surface of the liquid in the center compartment is held rigidly between two stiff micarta rings with a soft rubber packing on both sides. To minimize the danger of electric leakage and breakdown, both sides of the edge of the glass plate had first been covered with a thin layer of Apiezon W-100 sealing wax. Then the assembly was heated overnight at about 80°C. Before it cooled off to ordinary temperatures, the holding screws were tightened uniformly, squeezing out excess wax. To make the glass plate a little thinner it was etched overnight with 5% hydrofluoric acid. During the first trial of the reactor the electrical discharge drilled a hole in the glass plate but in the second attempt an evenly distributed discharge was obtained. The amount of formaldehyde generated at a current of 20 milliamperes and about 8.6 KV was, however, approximately the same as that formed using the tubular reactors. Raising the current caused breakdown of the insulation after a short time, but the glass disc was not punctured.

Before the above described reactor was completed, some experiments were run using a tubular reactor immersed in a water bath as shown on the left hand side of Figure 3 in the first chapter. This reactor is provided with a water-cooled center aluminum electrode and water could be introduced into the gas stream through a circular row of small holes drilled in the adapter used to hold it in place. The water was added by passing the gas stream through a heated bubbling column of glass. Some of the experiments gave relatively high yields, but again the reproducibility was poor due to the formation of larger droplets, giving a continuous, conducting liquid phase between the walls of the annular space of the reactor. To eliminate this source of error, the diameter of the lower end of the aluminum electrode, where most of the liquid formed accumulated, was decreased 0.125" over a distance of about two inches and three short Teflon rods were inserted at right angle to the main axis for exact centering inside the mantel tube. This seemed to eliminate a large share of the hold up of larger droplets. The subsequent experiments gave appreciably higher power yields than previously, but the reproducibility was still considered somewhat inadequate. In order to improve the

reproducibility, an all glass reactor having approximately the same dimensions but with a somewhat wider annular space was also used.

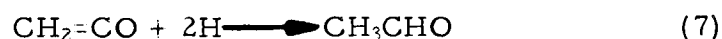
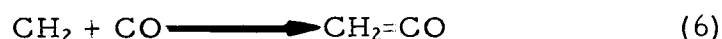
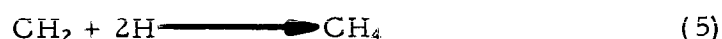
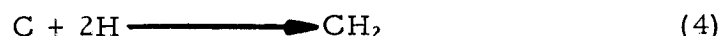
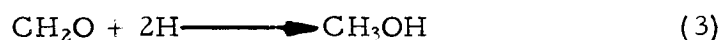
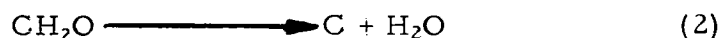
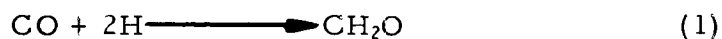
In Table 8 are given the data obtained from the tubular reactors, and Figure 7 shows the curves for the relative yields of formaldehyde as plotted against the current. Figure 8 shows the change of the voltage across these reactors as function of the current.

In Table 8 also are given some results obtained with a third tubular reactor which had been placed inside a long solenoid as shown in the center of Figure 3 of the first chapter. The yield data, which are plotted in Figure 9 show a surprisingly large effect of a comparatively weak magnetic field. Charge carriers moving in a magnetic field assume a circular motion and in combination with their linear velocity they will follow a helical path. Their angular velocity  $\omega$  may be expressed by the equation:

$$\omega = v / r = (e / m) B$$

where  $v$  is the linear velocity,  $r$  the radius of the circular path,  $e$  the charge,  $m$  the mass of the particle, and  $B$  the magnetic flux density, generally expressed in gauss. At high angular velocities of a charge carrier the probability of kinetically successful collisions should be enhanced, or in other words, the yield of a given reaction may increase.

Another effect has been noticed in the case of the aldehyde samples collected from the third tubular reactor. By polarographic analysis it was found that they generally contained minute quantities of acetaldehyde. The formation of this compound must take place through a series of steps. A wide range of reactions is possible and although the generation of formaldehyde is the main reaction it is conceivable that the following ones also take place;



The appearance of small amounts of hydrocarbons has been reported previously and the presence of traces of methyl alcohol also seems to be verified. The generation of acetaldehyde is of some interest since it can be separated from formaldehyde and reduced to ethanol.

The work with the several different reactors show that the yield of formaldehyde per KWH increases with current. The present electrical generating equipment limits the current to the level studied to date. The present budget does not provide for purchase of electrical generating equipment which would provide higher currents. Further work at higher current levels is essential to the full evaluation of this route for preparing formaldehyde.

### III. Tentative Conclusions Based on the Study of the Generation of Formaldehyde in Silent Discharges

Using tubular reactors the data obtained for the conversion of carbon monoxide mixed with hydrogen to give formaldehyde in a silent discharge have indicated the following results:

1. With increasing currents, increasingly larger amounts of formaldehyde are generated per KWH dissipated. This is illustrated graphically in Figure 9 in the case of two different reactors.
2. With decreasing thickness of the necessary dielectric layer, the power yield of formaldehyde increases proportionally. Using a single dielectric layer approximately doubles the yield obtained as compared with that of a reactor having two layers of the same thickness.

3. A number of data plotted in Figure 9 show that the presence of a magnetic field of increasing strength gives increasingly higher yields of formaldehyde.

From the study of the behavior of other chemical reactions in silent discharges, it may be inferred with a high degree of probability:

4. Size of active surface area and residence time of the gas stream in the reactor have a strong influence on the overall yield.
5. This effect is particularly important if the formaldehyde generated is absorbed continuously in water present in the reactor. In absence of water the yield decreases to zero, but the imposition of high frequency vibrations would be likely to distribute water present more uniformly and in the form of minute droplets causing any formaldehyde generated to absorb at a faster rate.
6. Lowering the pressure rapidly decreases the operating voltage and thus increases the power yield at a given current. It also decreases the power consumption in the first step of the process by lowering the compression ratio of the exit gas.
7. Lower temperatures in the reactor decrease the rate of decomposition of formaldehyde present in the gas phase and thus also increase the power yield.
8. The residence time of the gas stream in the reactor at a given flow rate varies with the diameter of the annular space, but this parameter also governs the overall effect of the charge carriers present.
9. The overall yield is known to vary with the frequency of the voltage impressed, but the rate of change is a characteristic function of the particular reaction studied.
10. With increasing power factor higher currents may be used at lower voltages to produce a given power input.

The adjustment of a dozen different variables to give best operating conditions is a highly complex problem that will require some time for a thorough understanding of the factors involved. The overall power yield

of formaldehyde has been roughly estimated and assumptions made as to the degree of improvement likely from a careful study of variables. Assuming a formose sugar yield of 60% the probable maximum yield indicated corresponds to a power consumption of about 0.7 KW per person present in the space cabin.

Table 1. Conversion of CO<sub>2</sub> to CO in DC Glow Discharge \*

A. Flow and Current Data

<u>Experiment</u>	<u>CO<sub>2</sub> flow l./min.</u>	<u>H<sub>2</sub> flow l./min.</u>	<u>Pressure mm Hg</u>	<u>Current amperes</u>	<u>Voltage KV</u>	<u>Power KW</u>
4-3-1	2	4	20	0.80	2.1	1.68
2	2	4	20	0.80	2.1	1.68
3	2	6	20	0.80	2.0	1.60
4	2	6	20	0.80	2.0	1.60
5	3	6	20	0.80	2.0	1.60
6	3	6	20	0.80	2.0	1.60
7	3	6	30	0.77	2.3	1.77
8	3	6	30	0.77	2.3	1.77
9	4	6	30	0.75	2.4	1.80
10	4	6	30	0.75	2.4	1.80
11	4	8	30	0.73	2.5	1.83
12	4	8	30	0.73	2.5	1.83

\* Reactor Figure 1, Chapter 1, copper, water-cooled electrodes, separation 25 cm. with center Vycor tube 2.66 cm. ID.

B. Analytical Data

<u>Experiment</u>	<u>H<sub>2</sub> Vol. %</u>	<u>H<sub>2</sub>O Vol. %</u>	<u>CO Vol. %</u>	<u>CO<sub>2</sub> Vol. %</u>	<u>Ratio CO/(CO + CO<sub>2</sub>)</u>
4-3-1	49	1.5	22	28	0.44
2	42	1.4	28	29	0.49
3	60	3	19	18	0.51
4	-	-	-	-	-
5	42	4	29	25	0.54
6	50	3	19	27	0.41
7	44.5	3.5	24.5	27.5	0.47
8	39	6	33	22	0.60
9	35	2	31	33	0.49
10	33	5	28	34	0.45
11	44	5	22	28	0.44
12	46	3	24	27	0.47
Average					0.48

Table 2. Conversion of CO<sub>2</sub> to CO in DC Glow Discharge \*

A. Flow and Current Data

<u>Experi- ment</u>	<u>CO<sub>2</sub> flow l./min.</u>	<u>H<sub>2</sub> flow l./min.</u>	<u>Pressure mm Hg</u>	<u>Current amperes</u>	<u>Voltage KV</u>	<u>Power KW</u>
4-4-1	3	4	35	0.75	2.3	1.73
2	3	4	35	0.75	2.3	1.73
3	3	6	35	0.73	2.4	1.75
4	3	6	35	0.73	2.4	1.75
5	4	6	35	0.73	2.5	1.82
6	4	6	35	0.73	2.5	1.82
7	4	8	35	0.73	2.5	1.82
8	4	8	35	0.71	2.6	1.85
9	5	8	35	0.70	2.7	1.89
10	5	8	35	0.70	2.7	1.89
11	5	10	35	0.69	2.8	1.93
12	5	10	35	0.69	2.8	1.93

\* Apparatus as in Table 1

B. Analytical Data

<u>Experi- ment</u>	<u>H<sub>2</sub> Vol. %</u>	<u>H<sub>2</sub>O Vol. %</u>	<u>CO Vol. %</u>	<u>CO<sub>2</sub> Vol. %</u>	<u>Ratio CO/(CO + CO<sub>2</sub>)</u>
4-4-1	38.4	3.5	24.3	33.8	0.42
2	38.5	2.5	24.2	34.6	0.41
3	51.5	2.4	23.5	22.5	0.51
4	49.4	2.7	24.9	23.0	0.52
5	43.0	3.1	24.2	29.7	0.45
6	43.7	3.6	23.1	29.6	0.44
7	45.0	2.7	24.8	27.4	0.48
8	47.3	3.0	22.5	27.2	0.45
9	40.2	2.6	23.0	34.1	0.40
10	32.6	4.0	25.0	38.5	0.43
11	39.2	2.6	23.6	32.4	0.42
12	42.5	2.4	22.6	32.5	0.41
Average					0.445

Table 3. Conversion of CO<sub>2</sub> to CO in DC Glow Discharge \*

A. Flow and Current Data

<u>Experi- ment</u>	<u>CO<sub>2</sub> flow l./min.</u>	<u>H<sub>2</sub> flow l./min.</u>	<u>Pressure mm Hg</u>	<u>Current amperes</u>	<u>Voltage KV</u>	<u>Power KW</u>
4-5-1	3	6	35	0.80	2.3	1.84
2	3	6	35	0.80	2.3	1.84
3	3	8	35	0.77	2.4	1.85
4	3	8	35	0.77	2.4	1.85
5	3	10	35	0.75	2.5	1.88
6	3	10	35	0.75	2.5	1.88
7	3	12	35	0.73	2.6	1.90
8	3	12	35	0.73	2.6	1.90
9	3	14	35	0.72	2.7	1.94
10	3	14	35	1.72	2.7	1.94
11	3	16	35	0.71	2.8	1.99
12	3	16	35	0.71	2.8	1.99

\* Reactor Figure 1, Chapter 1, water-cooled, copper cathode, carbon anode, 2.5 cm. dia., electrode separation 25 cm., using center Vycor tube, 2.66 cm. ID

B. Analytical Data

<u>Experi- ment</u>	<u>H<sub>2</sub> Vol. %</u>	<u>H<sub>2</sub>O Vol. %</u>	<u>CO Vol. %</u>	<u>CO<sub>2</sub> Vol. %</u>	<u>Ratio CO/(CO + CO<sub>2</sub>)</u>
4-5-1	59.8	0.31	2.9	37.0	0.073
2	59.9	0.24	3.3	36.6	0.083
3	67.0	0.40	3.4	29.2	0.104
4	67.0	0.44	3.4	29.2	0.104
5	69.5	0.36	3.2	26.9	0.107
6	72.9	0.43	2.9	23.8	0.112
7	76.6	0.36	2.6	20.4	0.115
8	76.4	0.27	2.6	20.7	0.115
9	79.1	0.22	2.3	18.5	0.112
10	78.0	0.21	2.2	19.6	0.101
11	80.9	0.29	2.0	16.9	0.106
12	80.7	0.26	2.0	17.0	0.105



Table 4. Conversion of CO<sub>2</sub> to CO in DC Glow Discharge \*

A. Flow and Current Data

<u>Experi- ment</u>	<u>CO<sub>2</sub> flow l./min.</u>	<u>H<sub>2</sub> flow l./min.</u>	<u>Pressure mm Hg</u>	<u>Current amperes</u>	<u>Voltage KV</u>	<u>Power KW</u>
4-6-1	3	6	25	0.72	2.1	1.51
2	3	6	30	0.69	2.3	1.59
3	3	6	35	0.67	2.5	1.67
4	3	6	40	0.62	2.7	1.67
5	3	8	25	0.65	2.6	1.69
6	3	8	30	0.63	2.7	1.70
7	3	8	35	0.60	2.9	1.74
8	3	8	40	0.57	3.0	1.71
9	3	10	25	0.62	2.7	1.67
10	3	10	30	0.59	2.9	1.71
11	3	10	35	0.57	3.0	1.71
12	3	10	40	0.55	3.2	1.76

\* Reactor Figure 1, Chapter 1, Vycor tube removed, water-cooled copper cathode, carbon anode, diam. 2.5 cm., electrode separation 25 cm.

B. Analytical Data for Above Runs

<u>Experi- ment</u>	<u>H<sub>2</sub> Vol. %</u>	<u>H<sub>2</sub>O Vol. %</u>	<u>CO Vol. %</u>	<u>CO<sub>2</sub> Vol. %</u>	<u>Ratio CO/(CO + CO<sub>2</sub>)</u>
4-6-1	41.0	4.5	38.4	16.0	0.706
2	39.9	4.8	39.4	15.9	0.713
3	39.4	5.2	40.2	15.2	0.716
4	35.8	5.6	43.2	15.4	0.739
5	54.0	3.8	28.3	13.8	0.672
6	55.8	3.6	28.0	12.6	0.690
7	51.4	5.6	30.5	12.4	0.711
8	52.6	5.2	31.1	11.0	0.739
9	62.2	4.1	21.6	12.1	0.642
10	62.0	3.3	23.4	11.3	0.674
11	61.3	4.0	23.8	10.9	0.686
12	61.0	3.3	24.5	11.2	0.687

Table 5. Conversion of CO<sub>2</sub> to CO in DC Glow Discharge \*

A. Flow and Current Data

<u>Experi- ment</u>	<u>CO<sub>2</sub> flow l/min.</u>	<u>H<sub>2</sub> flow l/min.</u>	<u>Pressure mm Hg</u>	<u>Current amperes</u>	<u>Voltage KV</u>	<u>Power KW</u>
4-9-1	3	6	20	0.80	2.4	1.92
2	3	6	25	0.77	2.6	2.00
3	3	6	30	0.77	2.7	2.08
4	3	6	35	0.80	2.5	2.00
5	3	6	40	0.78	2.6	2.03
6	3	3	20	0.77	2.0	1.54
7	3	3	25	0.78	2.0	1.56
8	3	3	30	0.76	2.2	1.67
9	3	3	35	0.76	2.4	1.82
10	3	3	40	0.74	2.5	1.85
11	3	4	20	0.80	2.0	1.60
12	3	4	25	0.78	2.1	1.64
13	3	4	30	0.76	2.3	1.75
14	3	4	35	0.75	2.4	1.80
15	3	4	40	0.72	2.6	1.87

\* Reactor, Figure 1, this chapter, water-cooled copper electrodes separation 25 cm., Reactor 0.875 in. ID

B. Analytical Data for Above Runs

<u>Experi- ment</u>	<u>H<sub>2</sub> Vol. %</u>	<u>H<sub>2</sub>O Vol. %</u>	<u>CO Vol. %</u>	<u>CO<sub>2</sub> Vol. %</u>	<u>Ratio CO/(CO + CO<sub>2</sub>)</u>
4-9-1	50.0	5.7	37.2	7.1	0.840
2	51.5	4.8	37.3	6.3	0.855
3	36.4	5.0	46.5	12.1	0.794
4	36.8	4.2	46.5	12.4	0.790
5	36.5	3.8	46.6	13.1	0.790
6	12.6	3.4	44.5	39.5	0.530
7	12.2	6.7	43.5	37.6	0.536
8	12.7	4.3	44.8	38.4	0.539
9	18.3	4.7	44.2	38.8	0.533
10	12.0	4.0	44.3	38.6	0.534
11	12.7	6.7	48.0	24.2	0.665
12	12.3	7.0	47.3	25.6	0.649
13	13.0	6.1	47.6	25.8	0.649
14	21.2	5.3	48.3	26.2	0.648
15	20.1	4.9	47.3	26.5	0.641

Table 6. Conversion of CO<sub>2</sub> to CO in DC Glow Discharge \*

A. Flow and Current Data

Experi- ment	CO <sub>2</sub> flow l/min.	H <sub>2</sub> flow l/min.	Pressure mm Hg	Current amperes	Voltage KV	Power KW
4-10-1	2	8	20	0.80	2.7	2.16
2	2	8	25	0.79	2.8	2.21
3	2	8	30	0.76	3.0	2.28
4	2	8	35	0.73	3.1	2.26
5	2	8	40	0.72	3.3	2.38
6	2	10	21	0.80	2.9	2.32
7	2	10	25	0.78	3.0	2.34
8	2	10	30	0.75	3.1	2.33
9	2	10	35	0.71	3.3	2.34
10	2	10	40	0.68	3.5	2.38
11	2	8	39	0.72	3.4	2.45
12	2	8	51	0.66	3.8	2.51
13	2	8	64	0.58	4.2	2.44
14	2	6	51	0.61	3.8	2.31
15	2	6	64	0.60	4.1	2.46

\* Reactor Figure 1, this chapter, water-cooled copper cathode, carbon anode 1.27 cm. dia., electrode separation 26.7 cm.

B. Analytical Data for Above Runs

Experi- ment	H <sub>2</sub> Vol. %	H <sub>2</sub> O Vol. %	CO Vol. %	CO <sub>2</sub> Vol. %	Ratio CO/(CO + CO <sub>2</sub> )
4-10-1	64.1	3.1	26.7	6.0	0.818
2	65.0	3.1	26.4	5.5	0.828
3	63.3	3.2	28.0	5.5	0.836
4	63.0	3.5	28.5	4.9	0.854
5	63.9	2.8	29.0	4.3	0.871
6	70.6	2.4	20.6	6.4	0.763
7	70.6	2.6	20.8	6.0	0.776
8	70.4	3.0	21.4	5.2	0.799
9	67.6	3.0	24.2	5.2	0.823
10	69.4	3.0	23.1	4.5	0.837
11	60.8	3.2	31.4	4.6	0.872
12	63.5	3.1	29.6	3.7	0.889
13	63.5	3.0	30.0	3.5	0.896
14	49.0	4.7	39.6	6.7	0.855
15	49.2	3.0	40.5	3.0	0.931

Table 7. Degree of Conversion of Carbon Dioxide in Hydrogen to Carbon Monoxide as a Function of Feed Composition.

Volume Feed Ratio <u>H<sub>2</sub>/CO<sub>2</sub></u>	Degree of Conversion, Volume Ratio <u>CO/(CO + CO<sub>2</sub>)</u>
1.0	0.534
1.3	0.650
2.0	0.814
3.0	0.893
4.0	0.864
5.0	0.800

Table 8. Conversion of CO and H<sub>2</sub> to Formaldehyde in a Silent Discharge Using Different Tubular Reactors.

- A. Dimensional Data for the Reactors: 1.-all glass, 2.-reactor with aluminum center tube, 3.-all glass reactor inside solenoid; field strength of the solenoid measured along center of Reactor 3 was found to be about 80 gauss at a current of 20 amperes. The measurement was made with a Rawson Gauss meter loaned by Princeton University; actual field strength may be higher because the gauss meter sensing element was not designed for our equipment.

Reactor, Number	<u>1</u>	<u>2</u>	<u>3</u>
Length of active surface area of center tube, cm.	80	91	115
Outer diameter of center tube, cm.	5.0	4.5	4.0
Outer diameter of mantel tube, cm.	6.3	5.3	6.0
Wall thickness of center tube, cm.	0.20	-	0.20
Wall thickness of mantel tube, cm.	0.24	0.23	0.24

B. Data Using Reactor 1

Current milliamp.	Voltage KV	H <sub>2</sub> flow l/min.	CO flow l/min.	Titer A * cc./hr.	Ratio A/(ma x KV)
44	9.7	2	2	17	0.040
60	10.2	2	2	32	0.052
80	11.4	2	2	42	0.046
100	12.2	2	2	99	0.081
110	13.0	2	2	156	0.109
124	13.3	2	2	256	0.156
110	11.7	3	1	146	0.113
110	11.5	4	1	127	0.100
110	13.2	3	1.5	128	0.088

\* Titer A represents the number of cc. of 0.088 N NaOH required to neutralize the amounts of HCOOH generated from CH<sub>2</sub>O when a sample is treated with 3% neutral hydrogen peroxide. Most of the data represent averages of two or more measurements.

C. Data Using Reactor 2

40	5.2	2	2	46	0.22
60	5.8	2	2	67	0.19
80	6.6	2	2	92	0.17
96	6.9	2	2	128	0.19
60	5.1	3	1	82	0.27
60	5.3	4	1	75	0.24

Table 8. (continued)

D. Data Using Reactor 3

a. zero magnetic field

<u>Current Milliamp.</u>	<u>Voltage KV</u>	<u>H<sub>2</sub> flow l/min.</u>	<u>CO flow l/min.</u>	<u>Titer A* cc./hr.</u>	<u>Ratio A/(ma x KV)</u>
60	13.5	2	2	91	0.112
80	14.6	2	2	153	0.131
100	14.7	2	2	207	0.141

b. magnetic field at least 40 gauss (10 amperes solenoid current)

60	13.6	2	2	130	0.159
80	14.6	2	2	185	0.159
100	15.7	2	2	246	0.157

c. magnetic field at least 60 gauss (15 amperes solenoid current)

60	13.6	2	2	147	0.180
80	14.6	2	2	235	0.201
100	15.6	2	2	293	0.188
60	12.5	3	1	171	0.228
60	12.1	4	1	207	0.285
80	13.6	4	1	203	0.188

E. Data Using Modified \*\* Reactor 2

60	6.9	2	2	38	0.145
80	7.6	2	2	86	0.142
90	7.8	2	2	99	0.141
110	8.0	2	2	179	0.204

\*\* A helical V groove with a pitch of 1.5", depth 1/8", width 1/4" was cut on surface of the aluminum center tube. Large amounts of liquid were held between the glass and aluminum surfaces in practically stationary positions along the top edge of the groove. The current appeared to be conducted mainly through the liquid phase and the yields of formaldehyde were both poor and nonreproducible. After decreasing the outer diameter of the aluminum tube with 0.125" no hold up of liquid occurred and the yield again became similar to the data from Reactor 2.

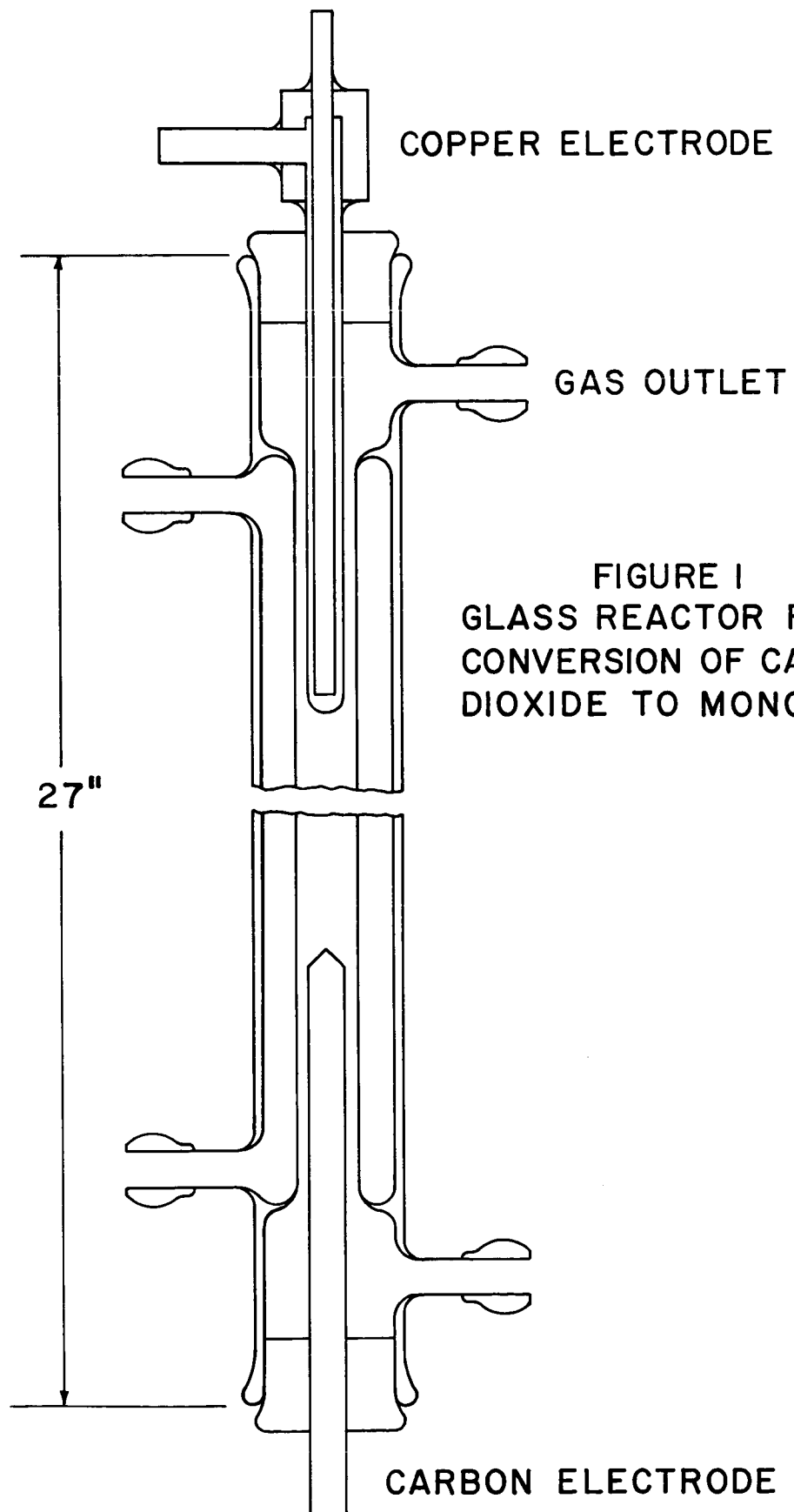


FIGURE I  
GLASS REACTOR FOR  
CONVERSION OF CARBON  
DIOXIDE TO MONOXIDE

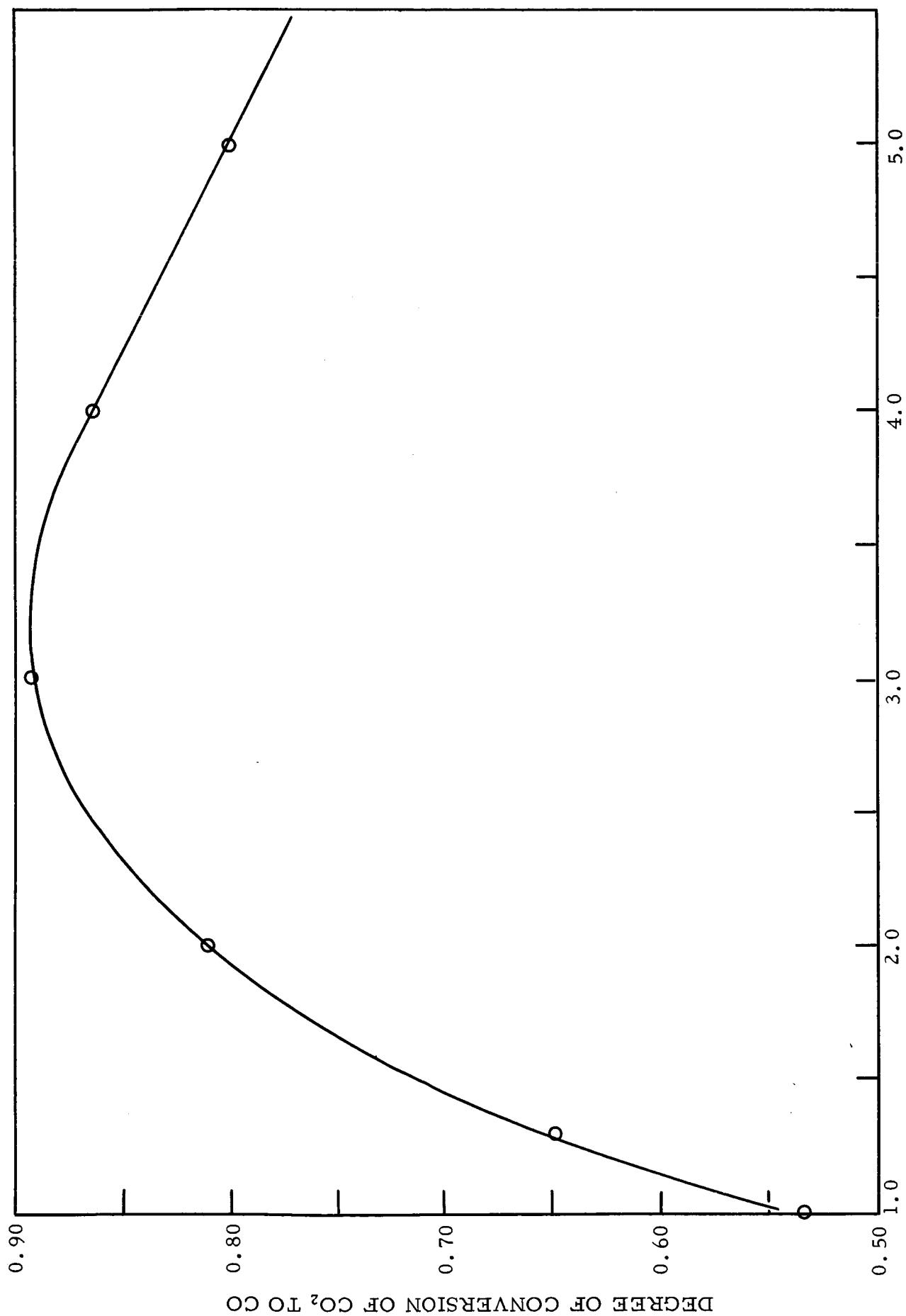
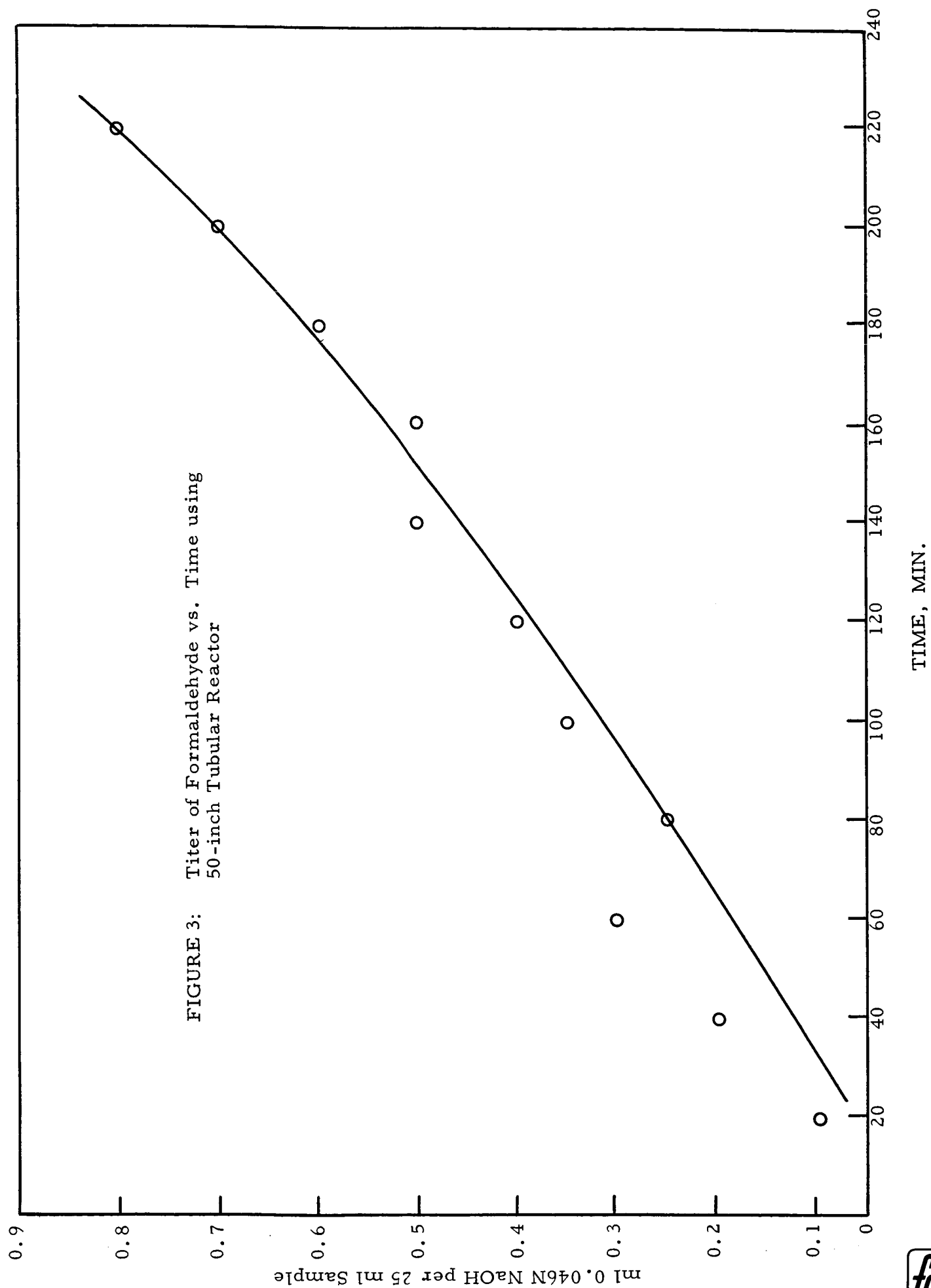


FIGURE 2: Degree of Conversion of CO<sub>2</sub> to CO as Function of the H<sub>2</sub>:CO<sub>2</sub> Ratio







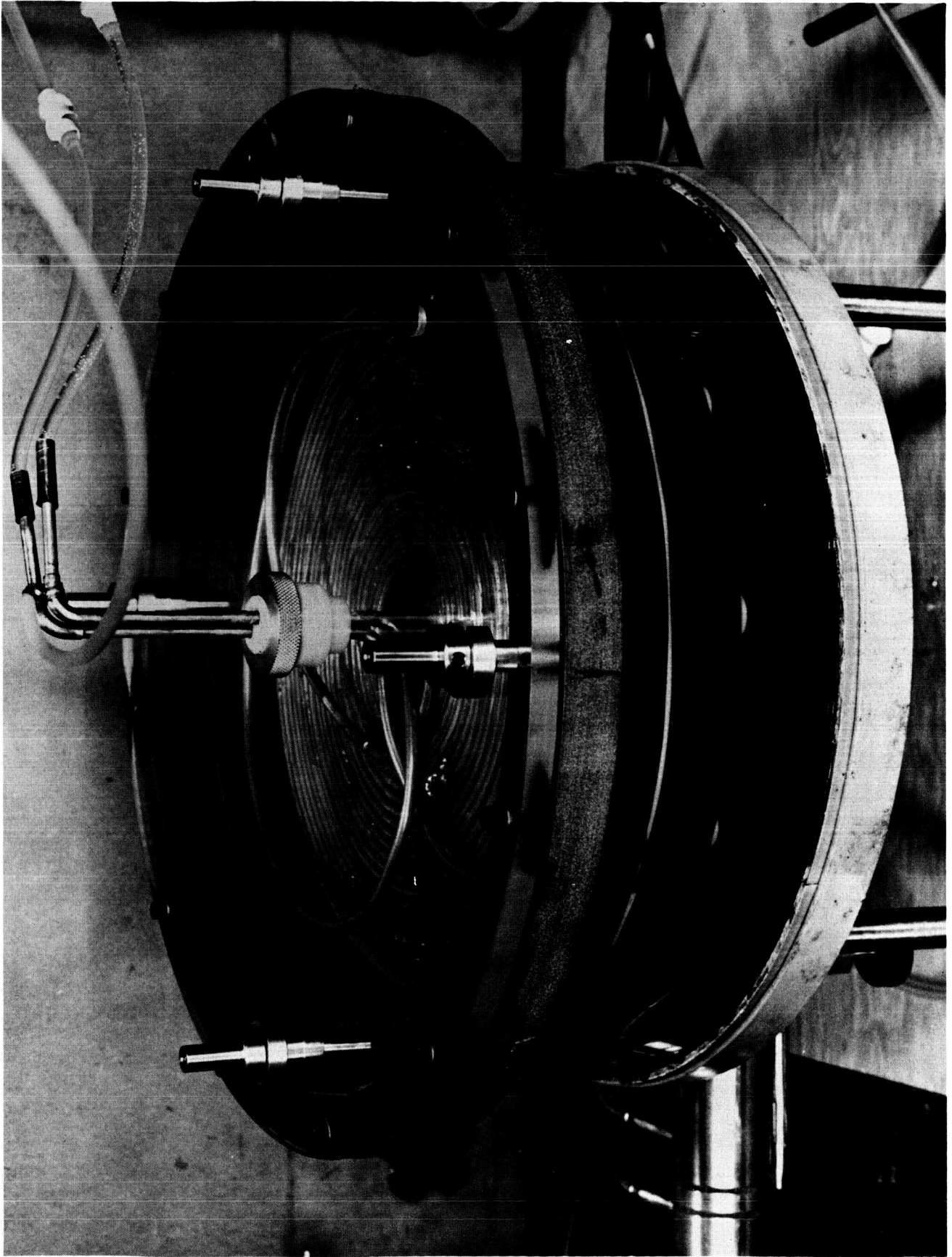


FIGURE 5: SILENT DISCHARGE REACTOR

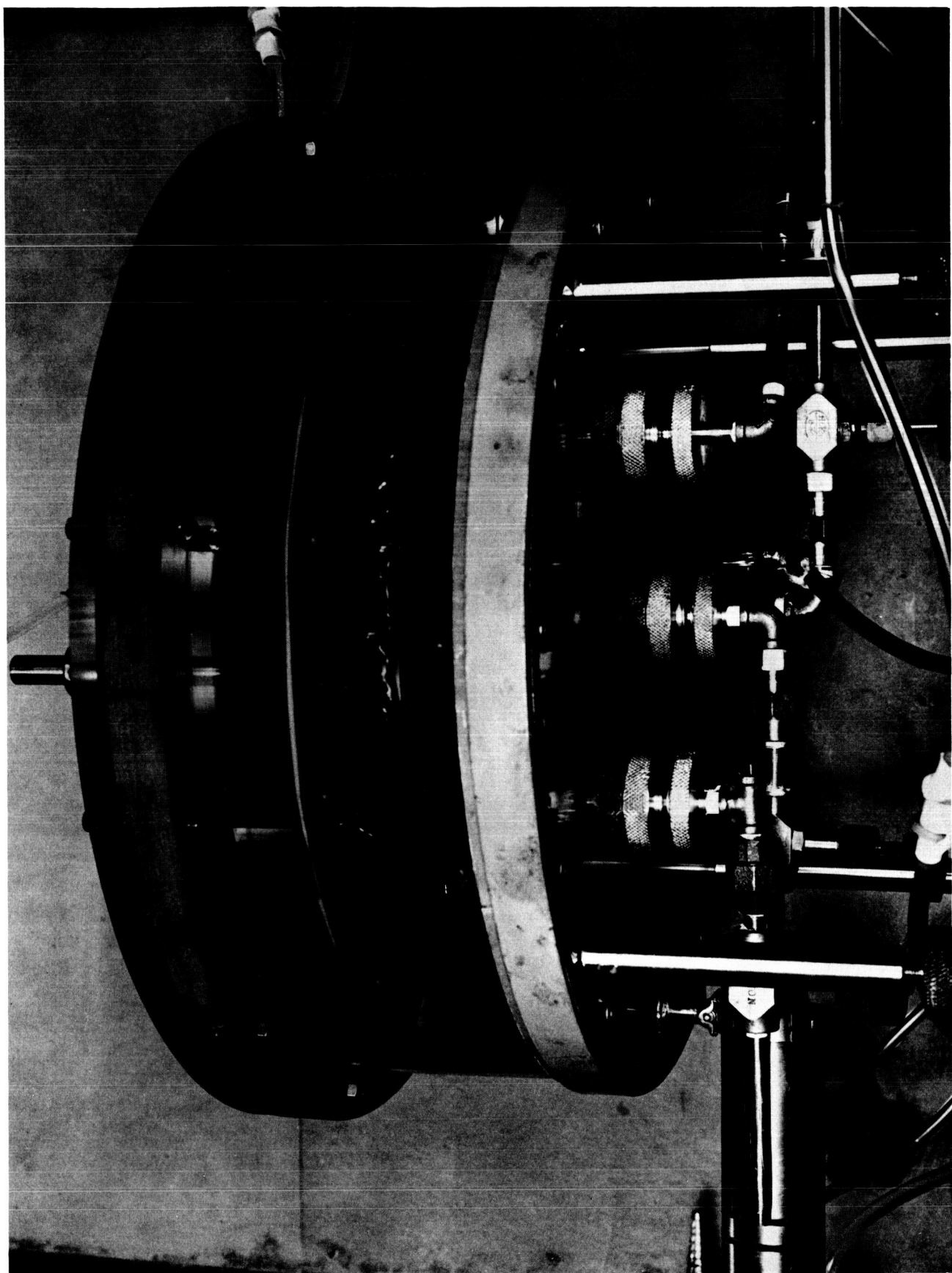


FIGURE 6: SILENT DISCHARGE REACTOR

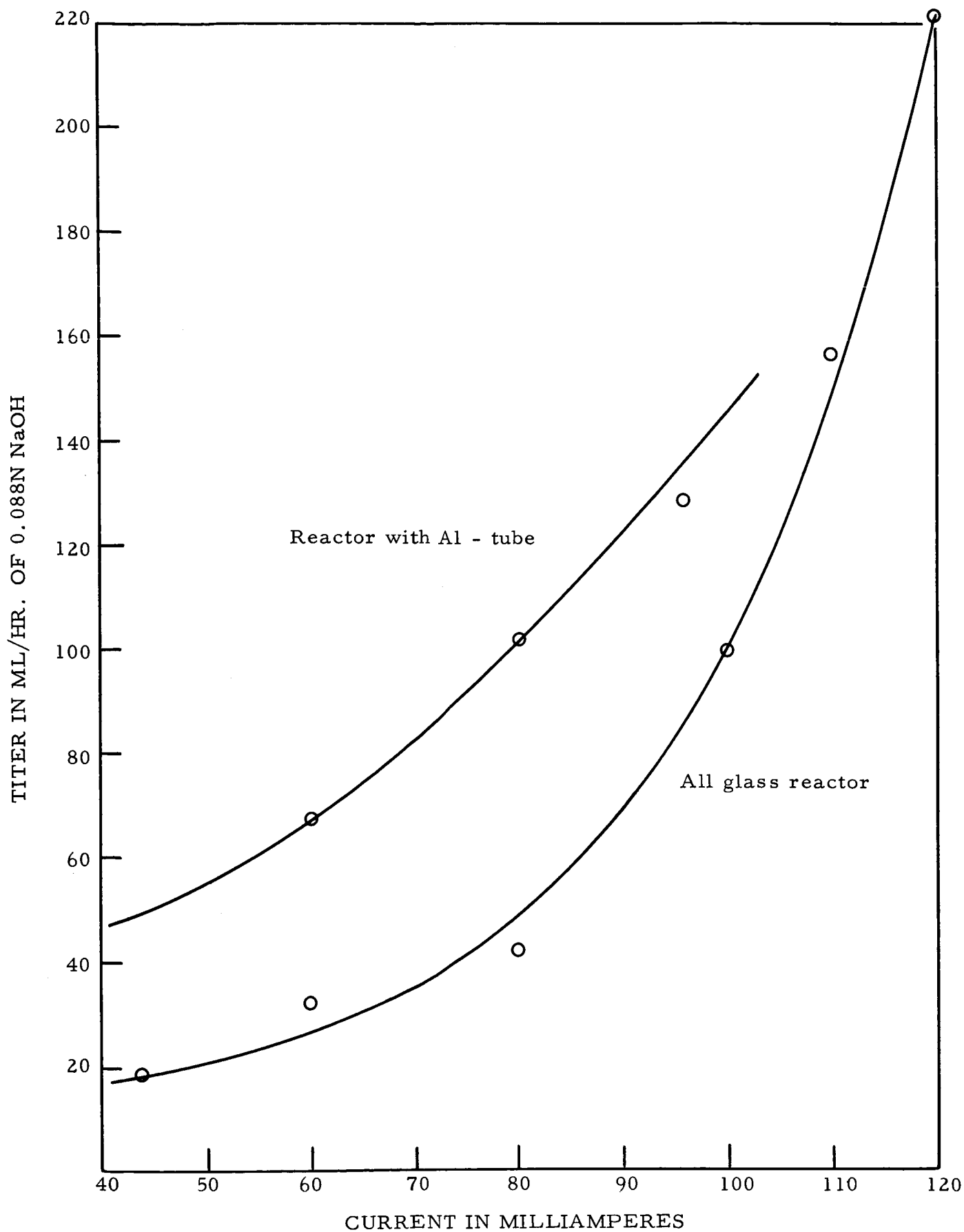


FIGURE 7: Amount of Formaldehyde Generated as Function of the Current (in relative units).

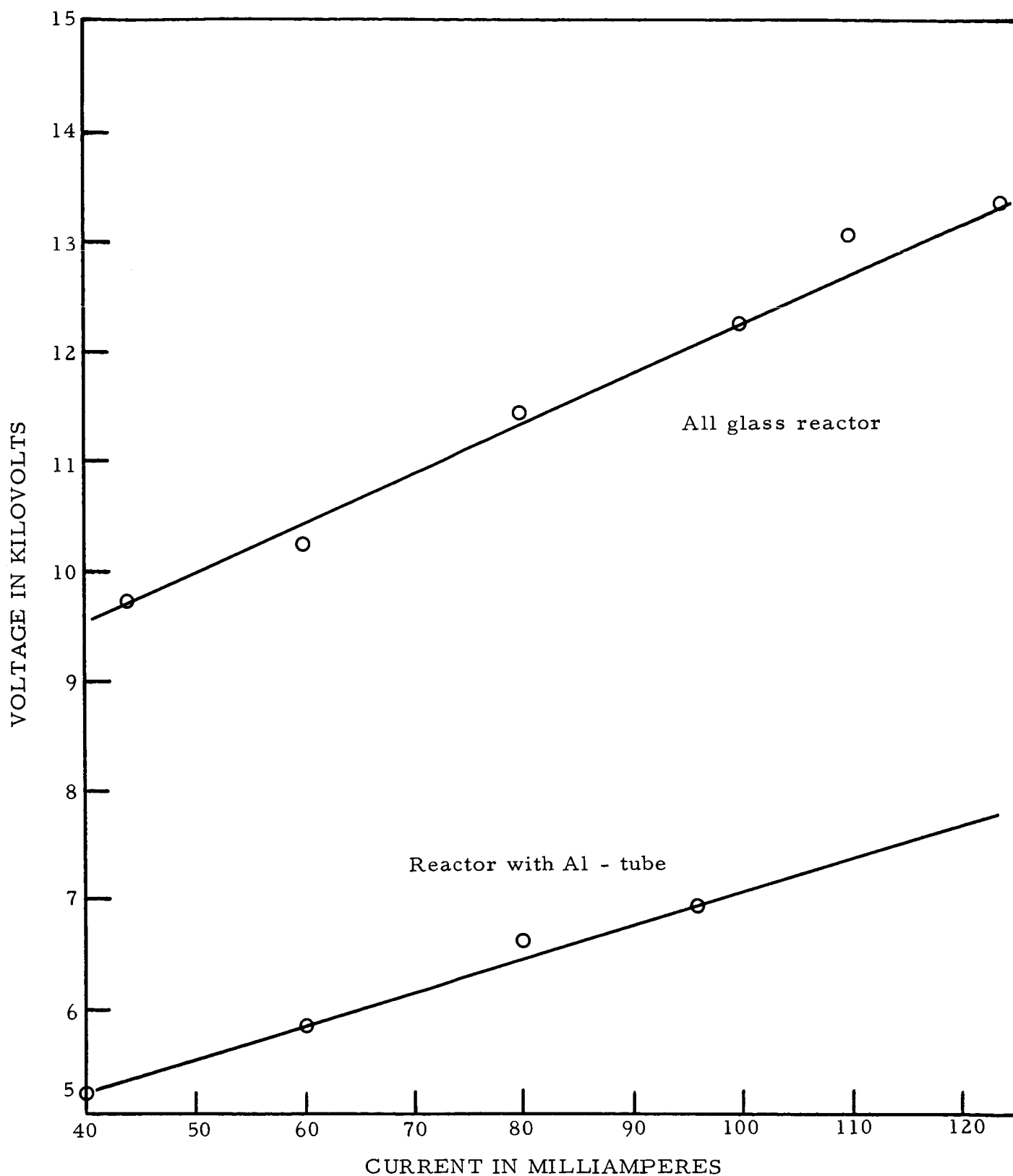


FIGURE 8: OPERATING VOLTAGE ACROSS DIFFERENT REACTORS AS PLOTTED AGAINST THE CURRENT.

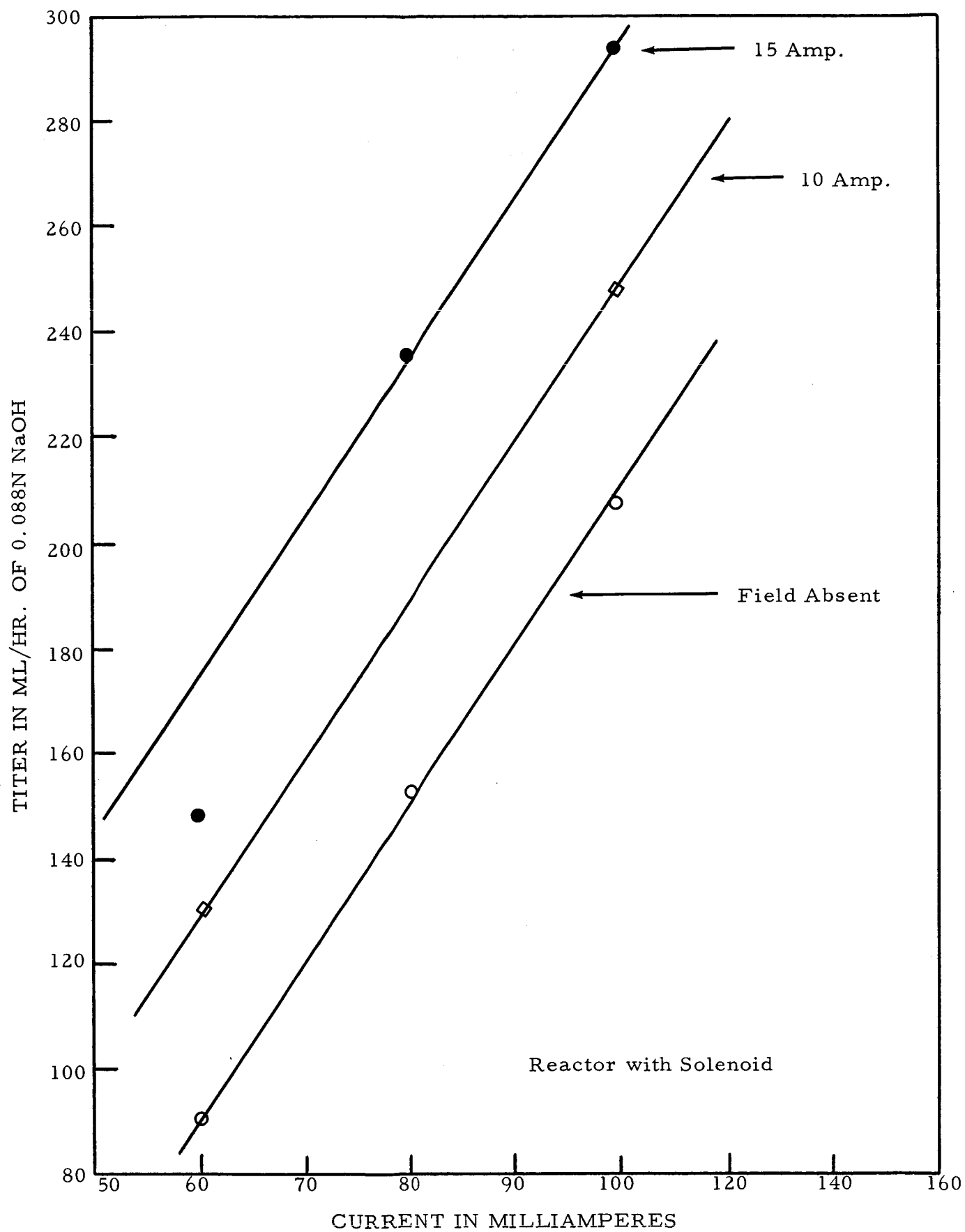


FIGURE 9

Relative Change in Yield of Formaldehyde at Different Magnetic Field Strengths.

### CHAPTER 3. GENERATION OF FORMALDEHYDE AS A FUNCTION OF VARIOUS FACTORS

#### Introduction

In this chapter is described work on the conversion of carbon monoxide to formaldehyde emphasizing various factors affecting the yield of this substance. The accuracy of the measurements has been improved considerably and an appreciable degree of chemical reproducibility has been found to be attainable. Good yields per unit discharge surface area are more readily obtained with a horizontal dielectric plate above an aqueous layer than in a tubular reactor where the gas stream is mixed with water vapor saturated at slightly elevated temperatures. The large effect of a magnetic field of moderate intensity on the yield of formaldehyde was re-verified.

The data obtained, particularly using a plate to liquid discharge strongly suggest the feasibility of producing sufficient quantities of formaldehyde to allow the generation of the carbohydrate requirements of the crew during extended travel in space. At weightlessness the discharge reactors must be operable in any position and a preliminary mathematical analysis has shown that this readily may be accomplished. A spinning, tapered, cylindrical reactor with an active surface area about 10 inches in diameter and 48 inches long may perhaps be able to produce about 3000 grams of formaldehyde per day.

#### I. Generation of Formaldehyde in a Silent Discharge Using an All Glass Reactor

##### 1. Analytical procedure for the determination of formaldehyde

Prior to carrying out the measurements included in this chapter more standard acid and alkali solutions were made up in quantities of about 18 liters each. The titer of both was matched to give identical values of 0.1333N and then a series of test titrations were made using a solution of trioxymethylene with accurately known concentration. An excess of 3% reagent hydrogen peroxide was added to each formaldehyde sample together with a measured amount of the standardized sodium hydroxide solution. After keeping the liquid at 60°C over a period of 20 minutes using a con-



trolled water bath, it was cooled and back titrated to neutrality. In Figure 1 have been plotted data for the back titrations of a series of samples containing increasing amounts of formaldehyde in direct proportion to the amount of alkali added. A straight line passing through the origin represents the data within ordinary experimental deviations to be expected showing that the amounts of alkali consumed is strictly proportional to the amount of formaldehyde present and also that the acid and alkali standard solutions were matched to have identical titers.

2. Yield of formaldehyde as a function of the gas flow rate

The main dimensions of the all-glass reactor used are given in Part A of Table 9 in Chapter 2. However, the walls enclosing the annular space of the reactor have been re-etched in order to lower their electric resistance and thus improve the yield of formaldehyde per KWH consumed. As before the incoming gas stream was bubbled through a twelve inches deep column of water, the temperature of which was held approximately constant and in the range of 60 to 80°C. The data obtained at constant power input and various flow rates are summarized in Table 1 and illustrated graphically in Figure 2. Without any apparent increase in the power consumption the yield of formaldehyde increases very rapidly with the flow rate. At a total flow of CO and H<sub>2</sub> of only 12 liters per minute and a recycle ratio of unity it is estimated that relative yields corresponding to well above 500 cc NaOH titer solution per hour probably would be attainable. The power factor of the discharge current is quite low and yields of 5 grams of formaldehyde per KWH dissipated seem assured.

3. Yield of formaldehyde as function of power input

Using the same reactor as before a number of yield data were obtained at different current values. The measurements are summarized in Table 2 and shown graphically in Figure 3 where the yield of formaldehyde is plotted as function of the current and Figure 4 where the latter is plotted against the voltage across the reactor. As discussed above a knowledge of the power factor involved is necessary before the

actual power input may be computed. However, it would seem to be probable that with a given reactor, circuit constants and fixed current frequency only minor changes of the power factor would occur over a wide current range. The observed large increases in yield of formaldehyde with increasing flow rate at constant power input should enable us to get very much higher yields than any measured so far at power and flow levels beyond our present reach.

4. Yield of formaldehyde as function of the ratio of the concentrations of the reactants

In Chapter 2 it was shown that when mixtures of hydrogen and carbon dioxide were exposed to a glow discharge under certain definite conditions maximum conversion to carbon monoxide and water was obtained when the ratio of the reacting gases was close to 3.0. The law of mass action requiring a ratio of unity is generally inapplicable to chemical reactions in glow discharges and it is doubtful if a thermodynamic equilibrium solely dependent on temperature is set up in any type of reaction taking place under similar circumstances. Since the generation of formaldehyde will be carried out using the gas mixture leaving the glow discharge reactor and without further changes in its composition it is important to know the concentration ratio of carbon monoxide and hydrogen at which maximum yield is obtained for a given power input and flow rate.

Table 3 summarizes the yield measurements carried out at a series of different ratios for the carbon monoxide and hydrogen concentrations at a constant total flow of 12 liters per minute while the power input was maintained at about the same level during all of the experiments. In Figure 5 the yield data have been plotted against the  $H_2/CO$  ratio to the left and the  $CO/H_2$  ratio to the right of the ratio of unity. The yield of formaldehyde shows a maximum at this ratio and declines somewhat asymmetrically to either side.

As a general rule the rate of any homogeneous chemical reaction taking place in an electric discharge is very high, with a half life of the order of fractions of a millisecond. This is probably also true in the case of the generation of formaldehyde. In the case of the data given in Figure 3 the residence time of the reacting gas mixtures at a

total flow of 12 liters per minute would be about six seconds. Since virtually complete equilibrium would be attained in a few milliseconds large increases in rate of flow could be tolerated to give steadily increasing yields of formaldehyde per unit of time. The problem is likely to shift over from that of generating formaldehyde to that of collecting this substance without appreciable losses at high re-cycle ratios.

5. Yield of formaldehyde as affected by an impressed magnetic field

In Chapter 2 a few measurements were described on the effect of a magnetic field on the yield of formaldehyde. These measurements have been repeated with greater precision and in general they do verify our earlier results. With increasing power input to the discharge, the yield increased rapidly, when a magnetic field was applied, above the corresponding values obtained in its absence. The effect may be induced partially due to change of the power factor of the discharge current and partially due to changes in the path described by the electrons as suggested previously. If this were the case a larger magnetic field effect with respect to the yield of formaldehyde would be likely to be found using a discharge current with a high initial power factor that may require less force for further approach to unity.

In Table 4 have been summarized the measurements of the yield of formaldehyde with varying power input, constant total gas flow and DC current for the generation of the magnetic field. In Figure 6 the yield data have been plotted as function of the power input together with the curve for the corresponding data given in Table 2 obtained in the absence of a magnetic field. As shown by Figure 6 the magnetic field effect decreases uniformly with decreasing power input to the discharge as could be expected. A few measurements of the analogous effect on the formation of ozone from oxygen carried out using the Welsbach Model C ozone meter as analyzer, showed an analogous increase in yield due to the magnetic field at an ozone concentration close to the upper end of the range of the meter. The power input to the discharge reactor was, however, small and would not in the case of the generation of formaldehyde have registered a significant increase in yield.

## II. Generation of Formaldehyde Using a Tubular Reactor with a Metal Center Electrode

The center tube of the all glass reactor was removed and substituted with a silver plated, water cooled brass tube having about the same outer diameter. The bottom end of the metal tube was shaped like a 90° cone and supported with a Teflon adapter that fitted snugly the outlet tube of the reactor and was provided with an expanded V-shaped top for exact centering and four deep grooves for passage of liquids and gases. The power factor of the discharge current was even lower than usual as shown by the low current and the equally low voltage in the primary coil of the high frequency variable transformer at substantial values for both in the discharge. However, at the same time the current through the reactor was difficult to regulate and easily exceeded 300 milliamperes when the discharge became activated.

In spite of the unusually low power factor relatively substantial yields were obtained as shown by the data summarized in Table 5 giving the result of measurements both with and without the presence of a magnetic field. As demonstrated graphically in Figure 7 appreciably higher yields were obtained in the former case.

## III. Generation of Formaldehyde in a Discharge Enclosed Between a Flat Glass Plate and an Aqueous Surface

A satisfactory method for sealing in the plate glass disc of the reactor finally was developed. Several test runs over periods of about one hour at currents above 100 milliamperes and voltages of about 14 KV did not cause breakdown. At the same time the water circulation system was improved by installing a Vanton pump with Teflon body. Great care was taken that the water flowed as uniformly as possible over the edge of the retaining ring (part 22 in Figure 4 of Chapter 2). The rate of flow of water was held at about one liter per minute, which was found to be essential to obtain uniformity. The distance between the top edge of the retaining ring and the underside of the etched glass plate was adjusted to 0.313 inch in the case of the measurements summarized in Table 6.

The actual distance between the glass plate and the water surface was naturally somewhat smaller but it could not be measured easily. Test runs with a somewhat smaller distance caused wetting of the glass disc and most of the current passed directly through the liquid. At a distance of 0.375 inch a beautiful, uniform, strongly luminous discharge was formed but the operating voltage increased to about 17 KV and puncture of the insulation occurred after a short time.

The data given in Table 6 and illustrated graphically in Figure 8 show yields of formaldehyde of the same order of magnitude as the highest values obtained with the all glass tubular reactor, but at the same time the discharge area in the former case was only 1100 cm<sup>2</sup> as compared to 1450 cm<sup>2</sup> for the latter one, a difference of about 24%. As will be discussed below, at weightlessness in outer space, it is necessary to employ a spinning reactor generating its own gravitational field and a coherent aqueous phase. The flat plate reactor simulates the behavior of such a space reactor and therefore its performance will be studied further in considerable detail.

#### IV. Principle of Design for Reactor to Operate at Weightlessness in Outer Space

At weightlessness the separation of gas and liquid states can no longer be accomplished by utilizing their density differences. A tubular reactor held in a fixed position is likely to be inoperable during extended travel in outer space unless such a separation can be maintained in the discharge reactor at all times and in any position. However, either by spinning the entire space vehicle or the individual components involved a radial centrifugal force is readily generated. This force acts in general like ordinary gravitation but in addition an appreciable Coriolis like component must be present and may have to be taken into consideration. It is believed the nearest approach to the successful operation in outer space of a silent discharge reactor containing a liquid phase is represented by one employing a dielectric plate suspended above the surface of the liquid.

Assume that a hollow cone with the taper  $\Theta$  and represented by the line AB in Figure 8 rotates around its free axis y at an angular velocity  $\omega$ . Liquid enters at A and leaves at B forming a layer of thickness  $\Delta_1$  on the surface of the cone. The equation of motion of the liquid may be expressed by the equation: \*

$$\nu \frac{\delta^2 u}{\delta X^2} = -\omega^2 R_y \sin \Theta \quad (1)$$

where  $\nu$  denotes the kinematic viscosity of the liquid and  $u$  is the velocity component in the direction of the flow. The volume  $V$  of liquid passing through the cone at a radius  $R_y$  is found to be:

$$V = 2\pi R_y^2 \cdot \frac{d^3}{3} \cdot \frac{\omega^2 \cdot \sin \Theta}{\nu} \quad (2)$$

where  $d$  represents the density of the liquid. The thickness  $\Delta_1$  of the layer of liquid formed on the inside of the surface of the cone is given by the expression:

$$\Delta_1 = \sqrt[3]{\frac{3 \cdot V \cdot \nu}{2\pi \cdot R_y^2 \cdot \omega^2 \cdot \sin \Theta}} \quad (3)$$

The mean residence time  $\tau$  of the liquid between two cross sections of the cone a distance  $L$  apart is equal to:

$$\tau = \frac{L}{R_a} \cdot \frac{3 \nu}{\omega^2 \sin \Theta} \cdot \left[ \frac{2\pi R_a \omega^2 \sin \Theta}{3 V \nu} \right]^{2/3} \quad (4)$$

\* The author is indebted to Professor Martin Summerfield of Princeton University for his help in deriving the equations presented.

where  $R_a$  represents the mean radius of the cone over the distance  $L$  between the cross sections chosen. With given velocity of rotation, taper, length and average diameter of the reactor we should thus, using pertinent yield data, be able to predict the formaldehyde concentration level attainable in the liquid phase over a given length of time at the gas flow rate chosen and the amount of power dissipated in the discharge. The spinning reactor envisioned for our purpose would be carried by sealed ball bearings, enclosed in a vacuum tight housing carrying in- and outlets for gas and liquid and it would be driven either by magnetic coupling to a rotor through the shell or with a Selsyn device.

V. Discussion of Data Presented with Respect to Similar Ones for Other Reactions

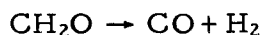
The measurements presented in this chapter may be summarized as follows:

- a. At constant power input the yield of formaldehyde increases strongly with the gas flow rate
- b. At constant gas flow rate the yield also increases strongly with increasing power input
- c. Maximum yield is attained when the reactants are present at equal concentrations, other conditions being constant.
- d. In the presence of a magnetic field the yield increases with both the power input and the flow rate

As yet we do not have any data on the effect of temperature, pressure and current frequency changes. We have previously emphasized that the power factor must be known under all conditions. Since two separate phases are present in the reactor it was questioned whether some purely physical factors like vibration would have any effect on the yield. A small vibrator (Model AA3, Viber Co., Burbank, California) driven with compressed air at 35 lbs. was fastened rigidly to the top end of the center metal electrode of the tubular reactor but measurements of the yield with and without vibration did not show a noticeable difference.

As a composite result we should be able to increase the yield of formaldehyde per unit of time to high values that would be limited only by the capacity of the reactor to tolerate the load, the voltage impressed and saturation phenomena that may complicate the picture. The simplest method to decrease the power load per unit active surface area consists of enlarging the reactor. It has previously been demonstrated by the author that in the case of the formation of hydrazine in a silent discharge a larger reactor will give within the limits studied substantially higher yields in direct proportion to the increase in surface area and without any evident increase in power consumption. The formation of hydrazine differs in many respects from the characteristics of the generation of formaldehyde but the effect of enlargement of the reactor surface area would seem to be a point in common.

Assuming monomolecular reactions it has been found that the rate of formation of hydrazine in a glow discharge is only a fraction of its rate of decomposition limiting sharply the overall yield attainable. In the analogous case for formaldehyde we have a better chance for higher yields since its decomposition regenerates the reactants:



A kinetic study of the overall rate of formation of formaldehyde would be valuable since it gives the basis for designing the minimum size reactor to be used for travel in outer space.



Table 1. Yield of Formaldehyde at Various Flow Rates, Constant Power Input and Gas Composition in All Glass Reactor.

Current ma	Voltage KV	Power KVA	Flow l./min.		Yield CH <sub>2</sub> O cc. NaOH*/hr.	Water °C
			CO	H <sub>2</sub>		
145	14.6	2.11	2	2	204	78
143	14.5	2.07	3	3	219	76
140	14.8	2.07	4	4	238	76
140	14.9	2.09	5	5	262	76
138	15.0	2.07	6	6	300	80

Table 2. Yield of Formaldehyde at Varying Power Input, Constant Flow and Gas Composition in All Glass Reactor.

Current ma	Voltage KV	Power KVA	Flow l./min.		Yield CH <sub>2</sub> O cc. NaOH*/hr.	Water °C
			CO	H <sub>2</sub>		
17	7.7	0.131	6	6	105	66
31	8.7	0.270	6	6	122	69
45	9.6	0.433	6	6	138	61
71	11.0	0.748	6	6	179	65
89	11.7	1.02	6	6	201	69
120	13.6	1.63	6	6	249	77
145	15.1	2.19	6	6	299	66
163	15.9	2.59	6	6	320	70

\* normality = 0.1333

Table 3. Yield of Formaldehyde with Varying CO to H<sub>2</sub> Ratio at Constant Total Flow and Power Input in All Glass Reactor.

Current ma	Voltage KV	Power KVA	Flow l./min.		Yield CH <sub>2</sub> O cc. NaOH/hr.**	Water °C
			CO	H <sub>2</sub>		
130	14.3	1.86	1.5	10.5	172	63
128	14.1	1.81	2	10	179	60
139	14.5	2.02	3	9	240	66
133	15.1	2.01	4	8	292	62
138	15.0	2.07	6	6	300	80
150	15.2	2.28*	8	4	305*	65
170	15.6	2.65	9	3	324*	68

\* Correcting the last two yield values to the average power input for the five preceding ones we obtain 287 and 244 respectively. Those two values have been used in plotting the curve shown in Figure 5.

\*\* normality = 0.1333

Table 4. Yield of Formaldehyde with Varying Power Input, Constant Total Flow and Magnetic Field Impressed in All Glass Reactor.

Current ma	Voltage KV	Power KVA	Flow l./min.		Yield CH <sub>2</sub> O cc. NaOH/hr.**	Water °C
			CO	H <sub>2</sub>		
40	8.2	0.328	6	6	104	63
38*	8.0	0.306	6	6	102*	71
44	8.5	0.374	6	6	123	62
61	10.3	0.628	6	6	167	73
81	12.2	0.988	6	6	222	61
109	14.5	1.58	6	6	323	65
131	15.9	2.08	6	6	339	63

\* No magnetic field applied. In all other experiments a DC current of 15 amperes was employed to generate the magnetic field.

\*\* normality = 0.1333

Table 5. Yield of Formaldehyde at Varying Gas Flow and Approximately Constant Power Input With and Without Magnetic Field Using Reactor with Center Metal Electrode.

A. <u>Measurements without field</u>						
<u>Current ma</u>	<u>Voltage KV</u>	<u>Power KVA</u>	<u>Flow l./min. CO      H<sub>2</sub></u>		<u>Yield CH<sub>2</sub>O cc. NaOH/hr.*</u>	<u>Water °C</u>
232	9.7	2.25	3	3	138	80
237	10.3	2.44	4	4	161	74
300+	10.4	3.12+	4	4	243	68
257	10.0	2.57	5	5	168	68
300+	10.4	3.12+	5	5	255	69
278	9.8	2.72	6	6	172	62
300+	10.4	3.12+	7	7	269	60
B. <u>Measurements with magnetic field</u>						
208	10.1	2.10	3	3	182	84
205	10.1	2.07	4	4	216	72
220	10.2	2.24	5	5	243	77
215	10.1	2.17	6	6	240	70

A DC current of 15 amperes was employed to generate the magnetic field

\* normality = 0.1333

Table 6. Yield of Formaldehyde at Varying Gas Flow Rates Using Reactor with Flat Glass Plate.

<u>Current ma</u>	<u>Voltage KV</u>	<u>Power KVA</u>	<u>Flow l./min. CO      H<sub>2</sub></u>		<u>Yield CH<sub>2</sub>O cc. NaOH/hr.*</u>	<u>Temp. °C</u>
124	13.9	1.72	2	2	240	28
122	13.2	1.61	4	4	290	28
138	13.4	1.85	6	6	320	28
136	13.2	1.79	8	8	360	28

\* normality = 0.1333

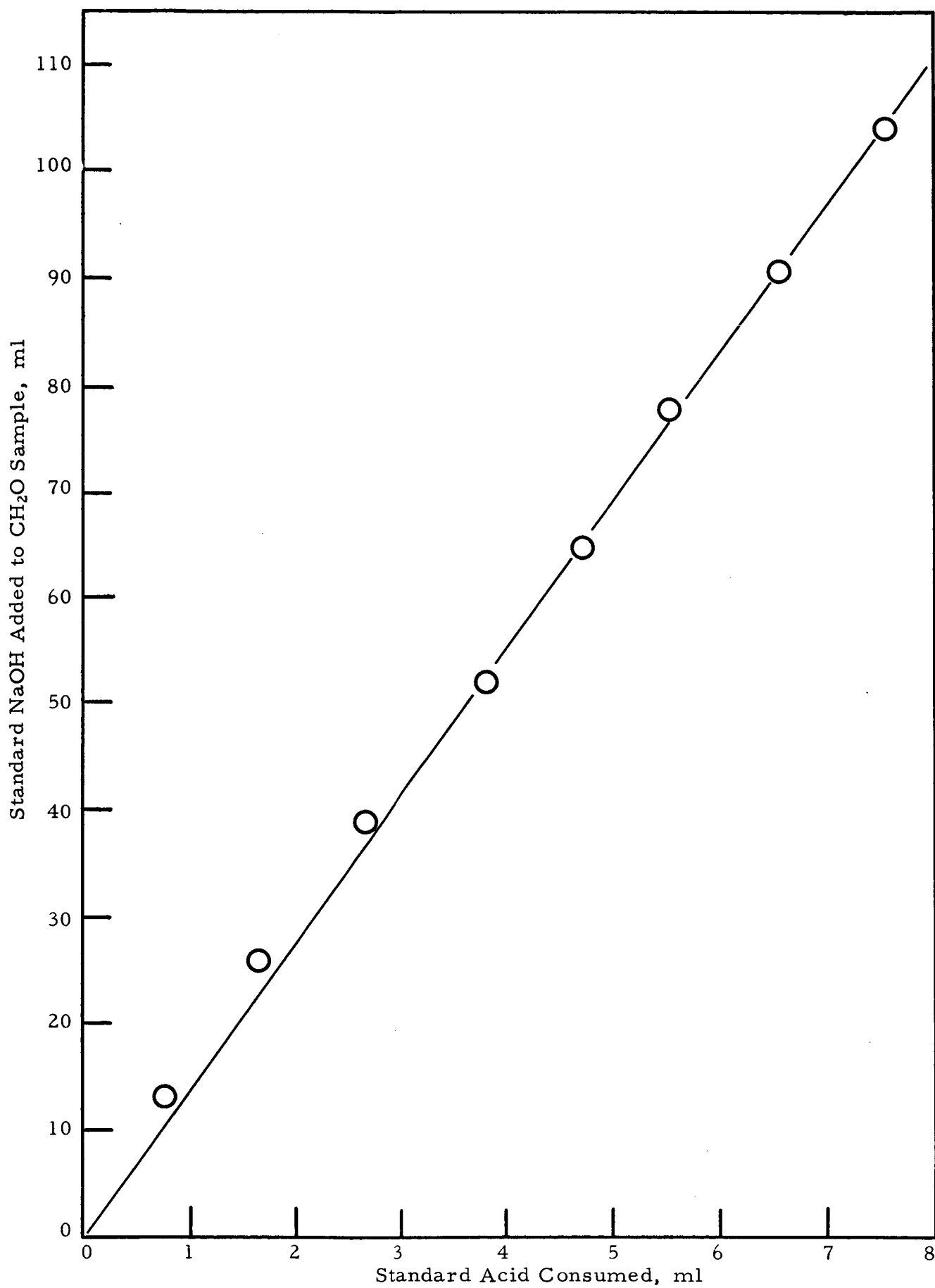


FIGURE 1. Test Back-Titrations of Solutions Containing Various Amounts of  $\text{CH}_2\text{O}$

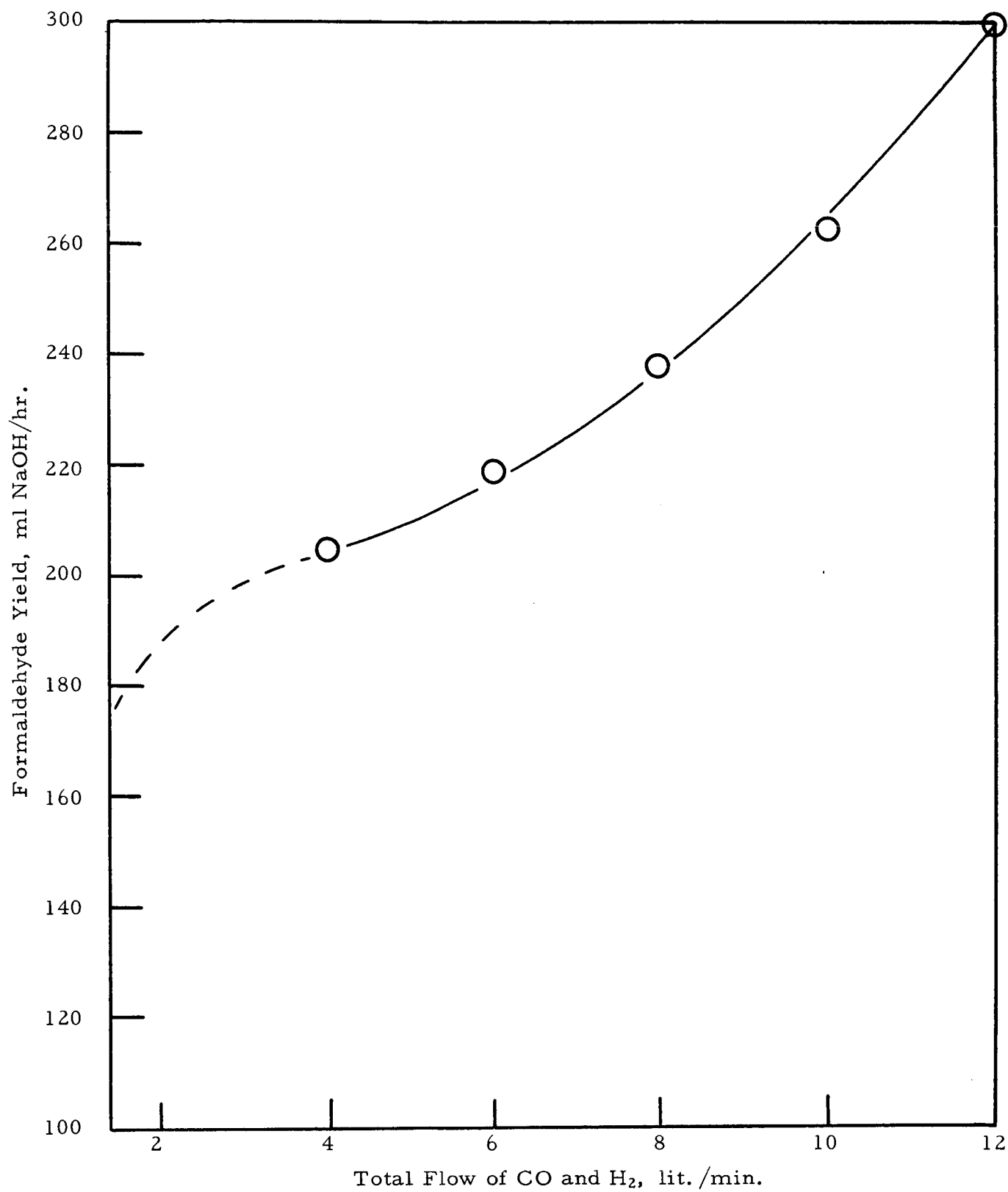


FIGURE 2. Yield of CH<sub>2</sub>O at Various Gas Flow Rates, Using the All-Glass Reactor

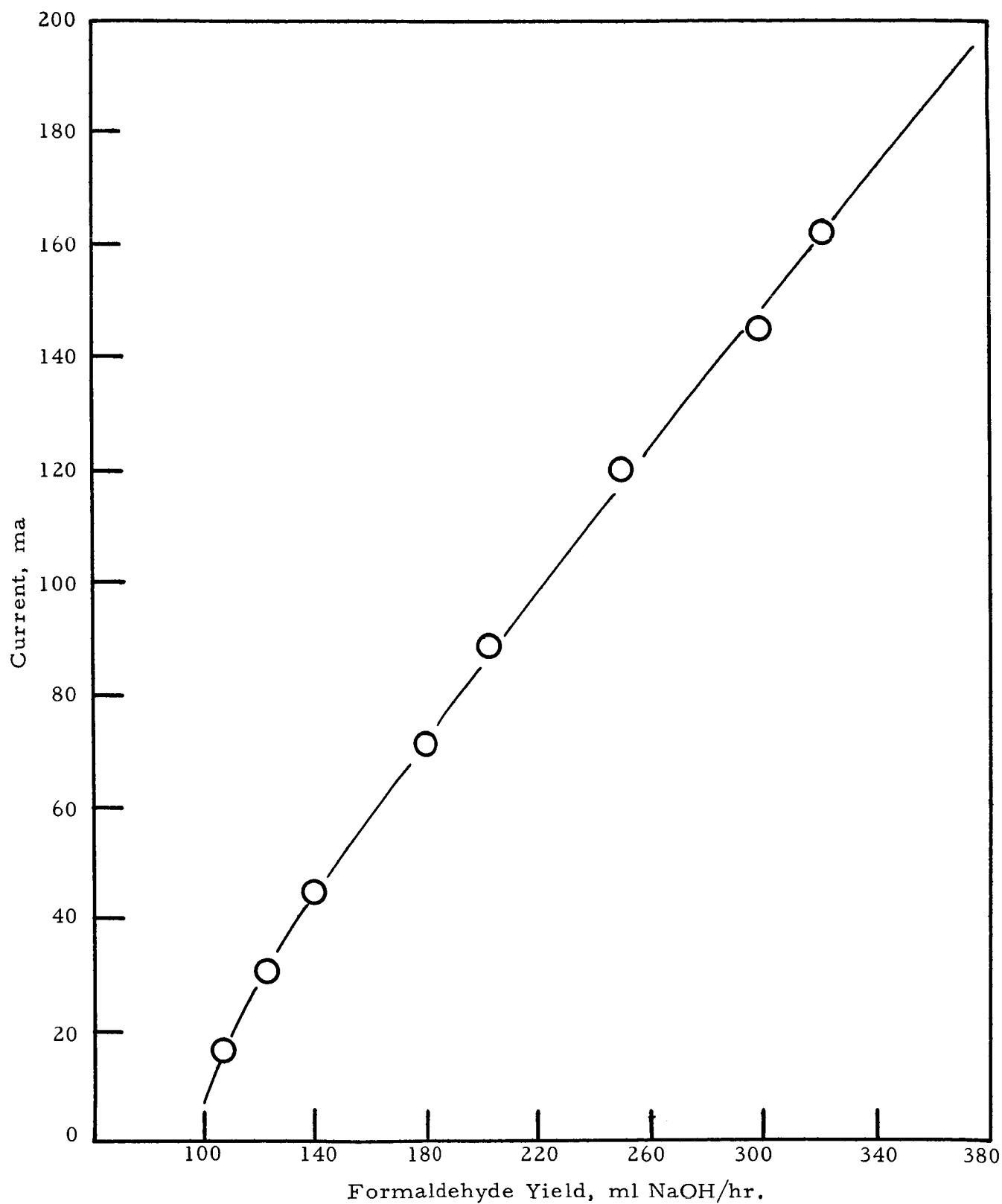


FIGURE 3. Relative Yield of Formaldehyde at Varying Current, Constant Flow and Gas Composition

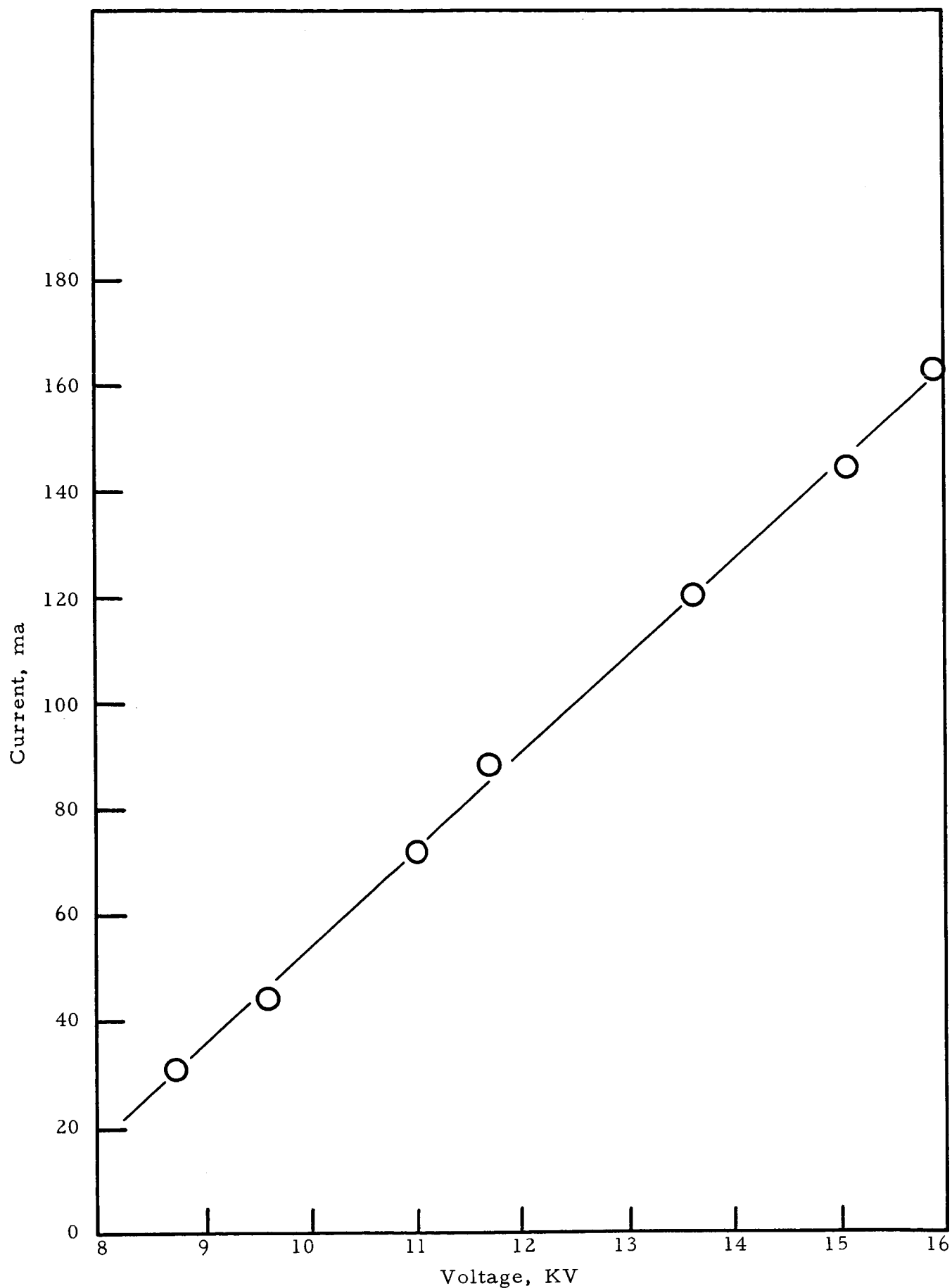


FIGURE 4. Current as Function of the Voltage at a CO or H<sub>2</sub> Flow of 6 lit./min, Using All-Glass Reactor

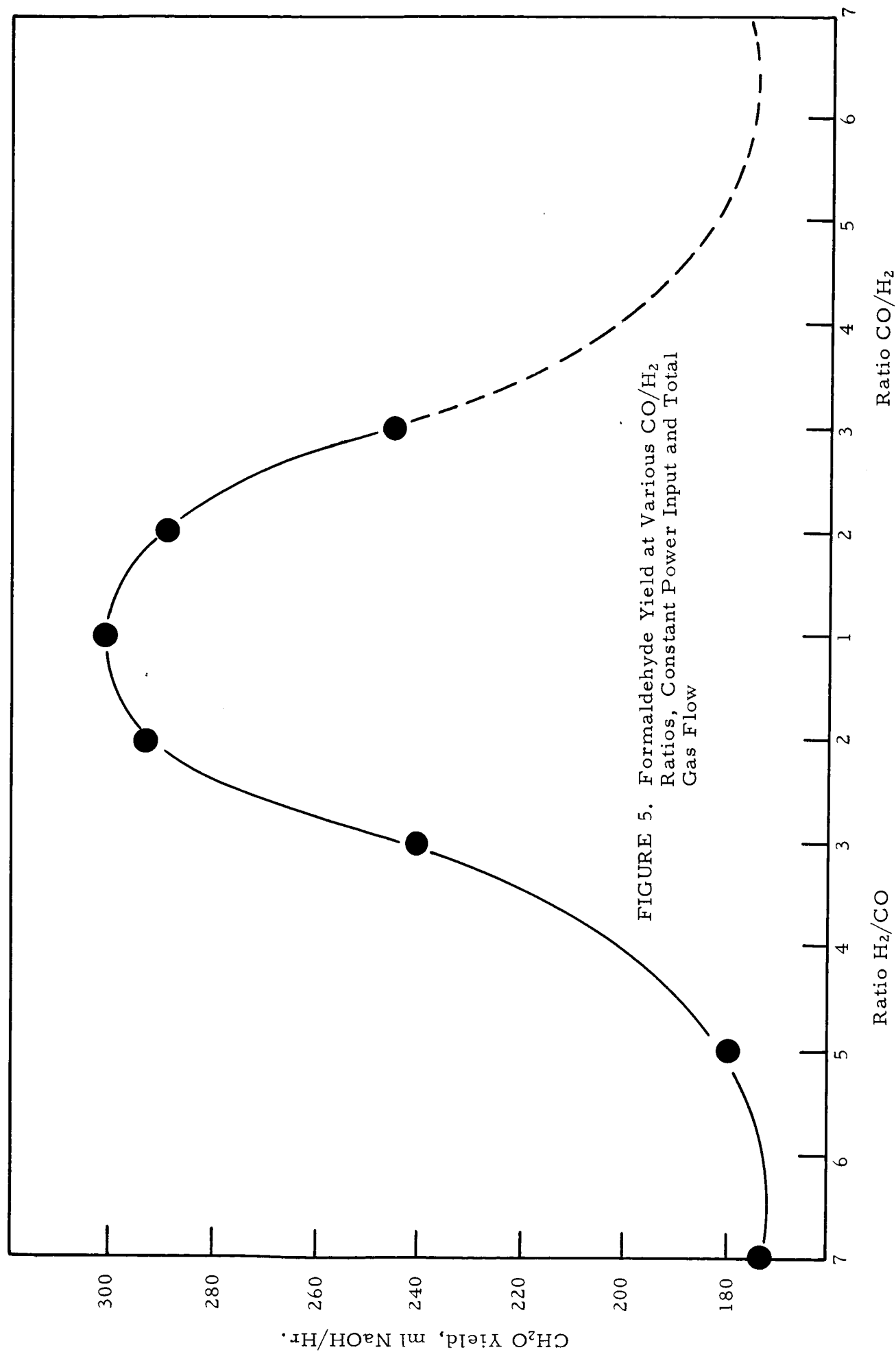
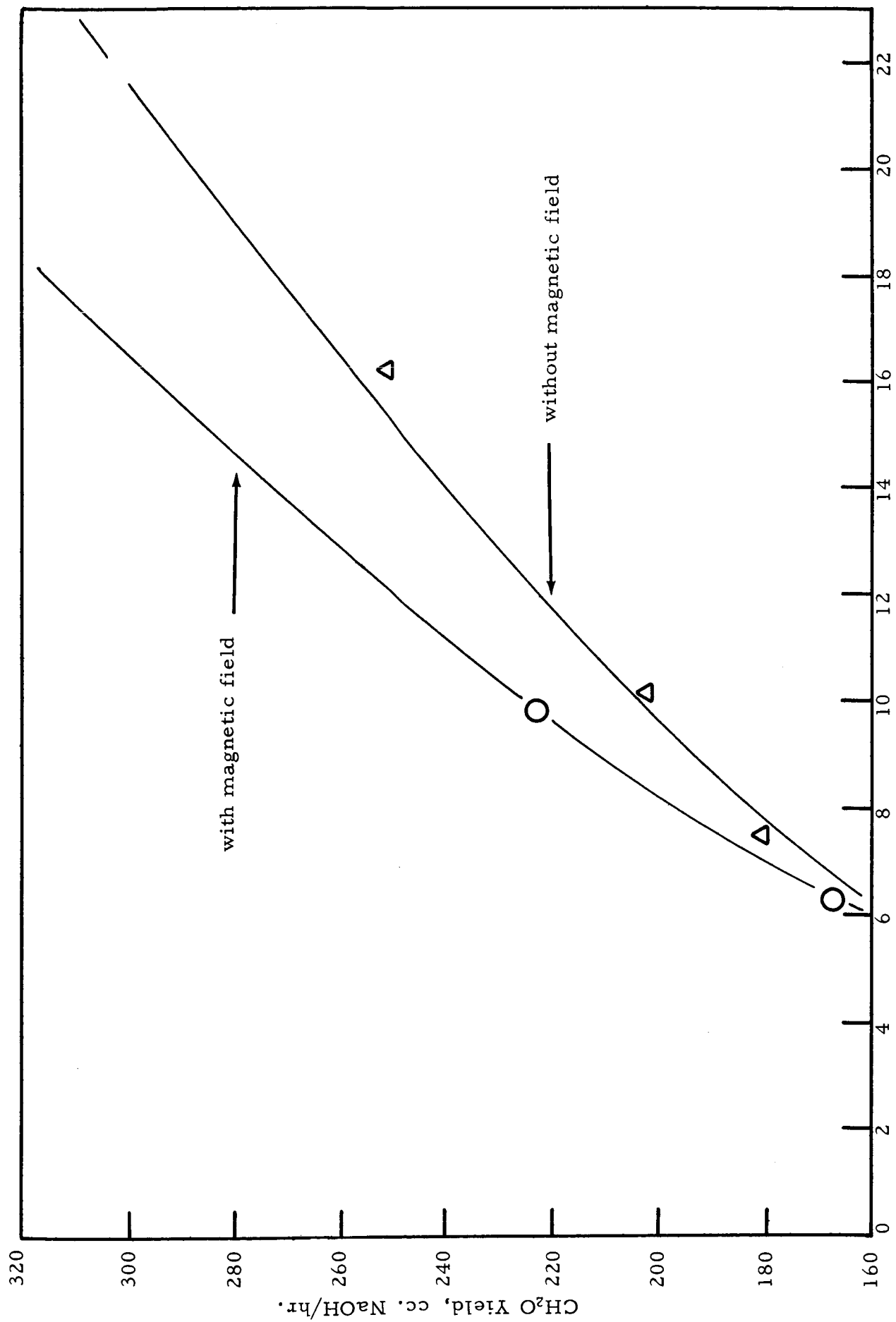


FIGURE 5. Formaldehyde Yield at Various CO/H<sub>2</sub> Ratios, Constant Power Input and Total Gas Flow





Power Input, KVA x 10<sup>-2</sup>

FIGURE 6. Relative Yield of CH<sub>2</sub>O as cc. NaOH/hr. at Various Power Inputs, With and Without Magnetic Field, Using All-Glass Reactor

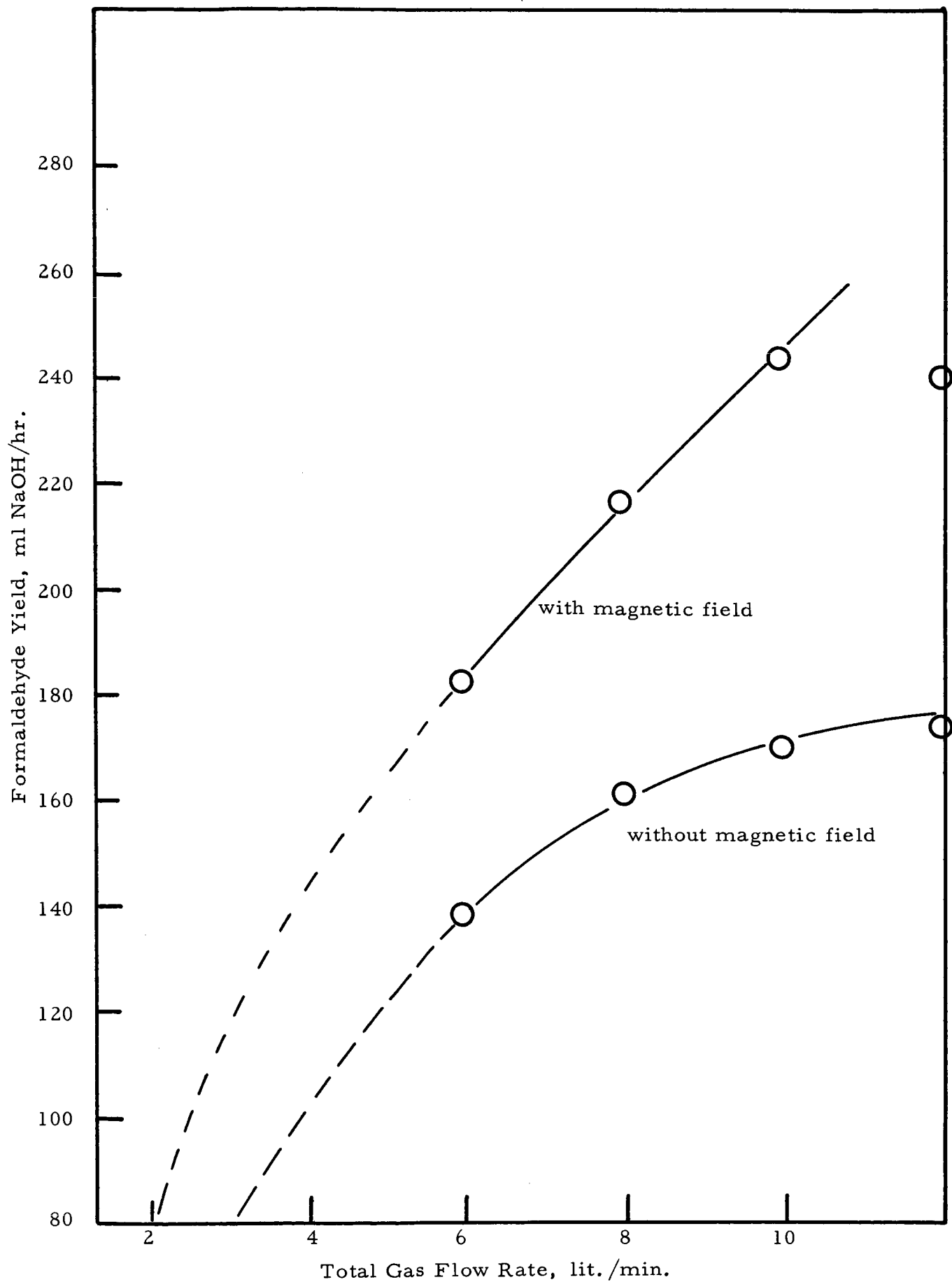


FIGURE 7. Yield of  $\text{CH}_2\text{O}$  at Various Flow Rates, With and Without Magnetic Field, Using Metal Center Electrode

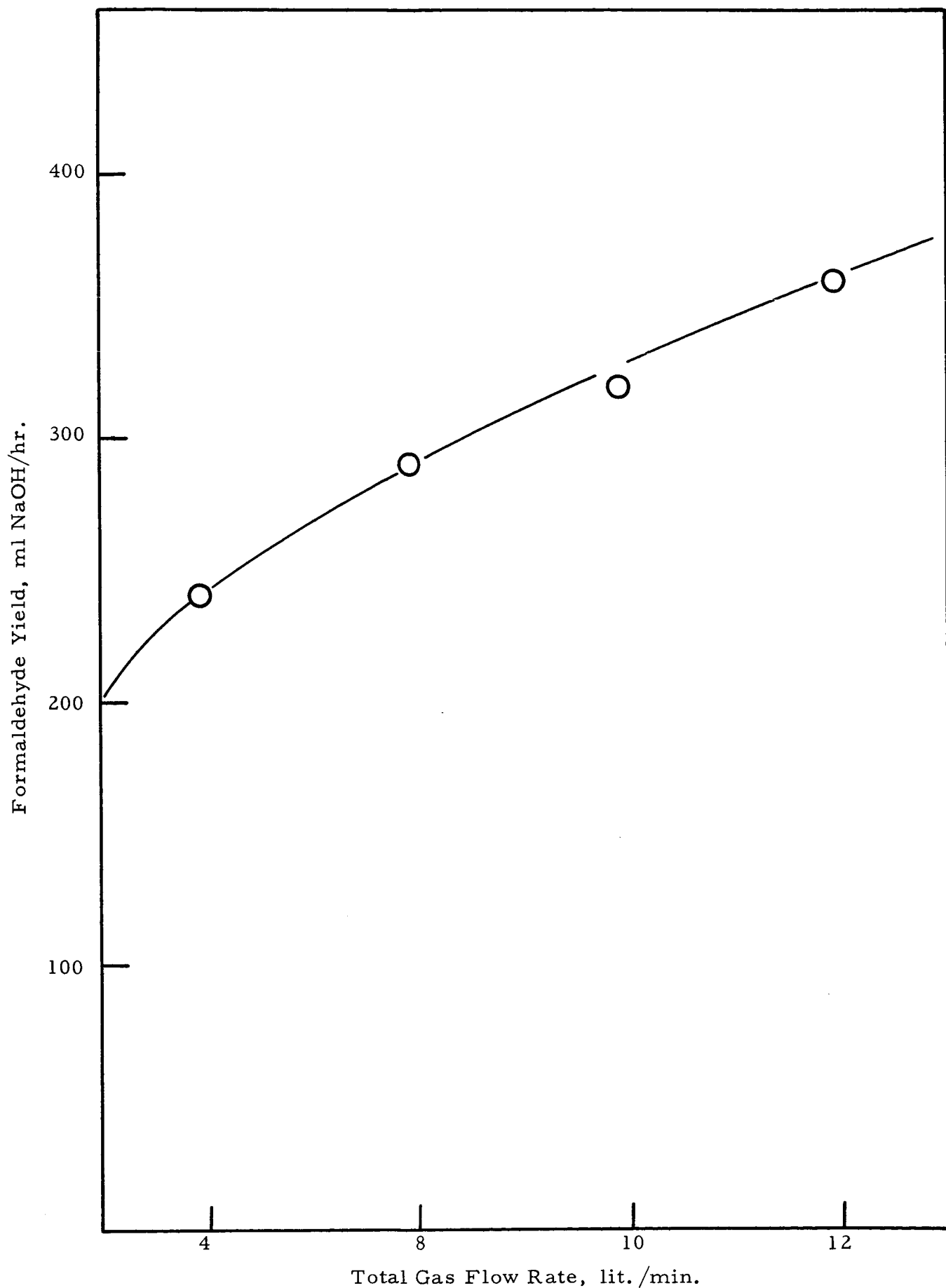


FIGURE 8. Yield of Formaldehyde at Various Gas Flow Rates, Using Reactor with Discharge Between Flat Plate and Flowing Liquid

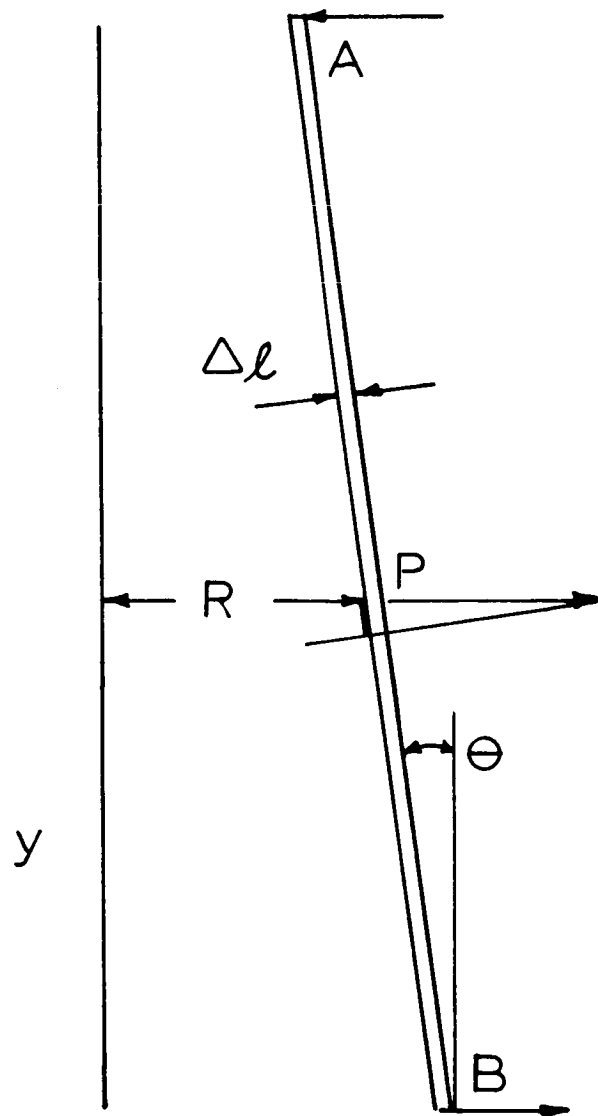


FIGURE 9. Principle of Tapered, Spinning Reactor

## CHAPTER 4. CONTINUOUS PRODUCTION OF FORMALDEHYDE FROM CARBON DIOXIDE AND HYDROGEN IN A CLOSED SYSTEM

---

### Introduction

A large laboratory unit has been built for the continuous production of formaldehyde from carbon dioxide and hydrogen in a closed system at steady state. Provision has been made for re-cycling of the gas stream from the silent discharge reactor and also to divert part of this recycle gas to the glow discharge in order to lower its carbon dioxide content, which tends to increase due to steady removal of carbon monoxide and hydrogen as formaldehyde dissolved in water.

A new tubular and also a new flat plate reactor have been built. Both should come within a factor of two or three to be able to produce sufficient formaldehyde to give, when self-condensed, an adequate amount of carbohydrates for a crew of five assuming that 50 % of the sugar is non-nutritional. However, the dilution effect of non-converted carbon dioxide from the glow discharge is likely to lower the yield of formaldehyde to some extent.

The direct conversion of carbon monoxide with hydrogen in a glow discharge to give graphite and water has been indicated. The use of this process might be necessary in case of temporary breakdown of the generation of formaldehyde.

### I. Principles of Operation

It is assumed that as carbon dioxide is liberated in a closed circuit respiratory system it may be removed from the atmosphere at about the same rate it is formed, more or less quantitatively, and isolated as a pure substance. There are several purely physical methods available to achieve the separation of the carbon dioxide but the particular method employed is immaterial for our purposes.

The carbon dioxide isolated will be fed into the processing system at such a rate that it will be converted quantitatively to formaldehyde which later would be generated in a definite amount per unit of time. This entails that the first step of the process, the reduction of the carbon dioxide to

monoxide with hydrogen in a glow discharge is adjusted to the rate of formation of formaldehyde in the second step by reacting the monoxide with excess hydrogen from the first reaction in a silent discharge. The amount of formaldehyde generated per pass of the gas mixture coming from the glow discharge is a complex function of a number of parameters like the dimensions of the reactor, current voltage, frequency and wave form, gas flow rate, composition, temperature and pressure. In general, however, since the rate of formation of formaldehyde is very much smaller than that of carbon monoxide the gas mixture passing through the silent discharge must be recycled several times in order to keep the two reactions in step with each other. At approximately constant power consumption the yield of formaldehyde per unit of time increases proportionately with the flow rate. The yield is also roughly proportional to the power input and adjustment of the two reactions with respect to each other should not on this account offer any particular difficulties. However, due to the necessity of re-cycling, another factor must be taken into consideration. To obtain maximum degree of conversion of carbon dioxide to the monoxide it is essential that the ratio of the concentrations of hydrogen and carbon dioxide in the reactor feed gas is equal to about 3. The generation of formaldehyde requires a reactant volume ratio equal to unity to attain maximum yield. Thus not only must a compromise be made between the reactant ratios of the two reactions but a further adjustment must be made with regard to the amount of power dissipated in the case of each reaction. At a degree of conversion of carbon dioxide to the monoxide of 80% the amount of power consumed is only about one-third of the amount dissipated to attain a conversion of 90%. Operating the glow discharge reactor to give a lower degree of conversion but a high power yield will necessitate that the formaldehyde is generated at a correspondingly higher power input using a reactor with large active surface area and as low a re-cycle ratio as possible. Although the amount of carbon dioxide present in the re-cycle gas mixture is reduced to some extent to carbon monoxide in a silent discharge, its concentrations will increase steadily. Thus part of the recycle gas must continuously be returned to the glow discharge in order to keep the concentration of carbon dioxide in the silent discharge

at a sufficiently low level to prevent appreciable interference with the generation of formaldehyde. The increase in the amount of power that must be dissipated in the glow discharge will be small. To minimize losses of formaldehyde generated it is essential that ample amounts of water are introduced for its absorption and also that the temperature of the exit gas stream from the silent discharge is lowered, preferably to zero degree C, before it re-enters the reactor.

## II. Design of Flow System

In Figure 1 are shown block diagrams of the flow systems for both gas and liquid phases present. Carbon dioxide and hydrogen enter the system through flowmeters  $F_1$  and  $F_2$ , pass in order through the glow discharge at some pressure  $P$  below atmosphere, a vacuum pump, a filter tank where any oil droplets from the pump are removed. After elimination of air at start-up using gas bleeds numbers 1 and 2 as controlled by analysis of samples taken at positions numbers 1 and 2, the gas mixture passes through flowmeter  $F_4$  to enter the tubular silent discharge reactor. Flowmeters  $F_5$  and  $F_6$  have been provided for measurements of the generation of formaldehyde using the pure reactants while  $F_7$  determines the re-cycle ratio using analytical data from sample taken at position number 4 to compute the average molecular weight of the gas stream.

Water may be introduced in the silent discharge in several different ways as will be discussed below and the formaldehyde solution formed will be re-circulated, given a well defined temperature before it re-enters by passing through heat exchangers numbers 2 and 3 and metered employing flowmeters  $F_8$  and  $F_9$ . The gas stream may also be moistened by bubbling through a water column maintained at constant temperature and provided with a steady feed of distilled water through flowmeter  $F_{10}$ . The liquid phase drains from the reactor into a small, welded stainless steel tank provided with bottom outlets to the circulating pump and for taking samples of the liquid. The gas stream entering this tank is led off to heat exchanger number 1 where it is cooled off to  $0^\circ\text{C}$  and then in order passes through a stainless steel tank with an inner volume of about

16.4 liters, an oil-less compressor, a second gas tank of the same size as the first one and finally flowmeter F<sub>7</sub> to re-enter the discharge reactor. Bleed number 3 allows purging of the air in this part of the system at start up. All bleeds are connected together and properly vented. To facilitate operation and give the necessary pressure readings, four manometers have been distributed at various points in the flow system.



### B. Liquid Flow Diagram

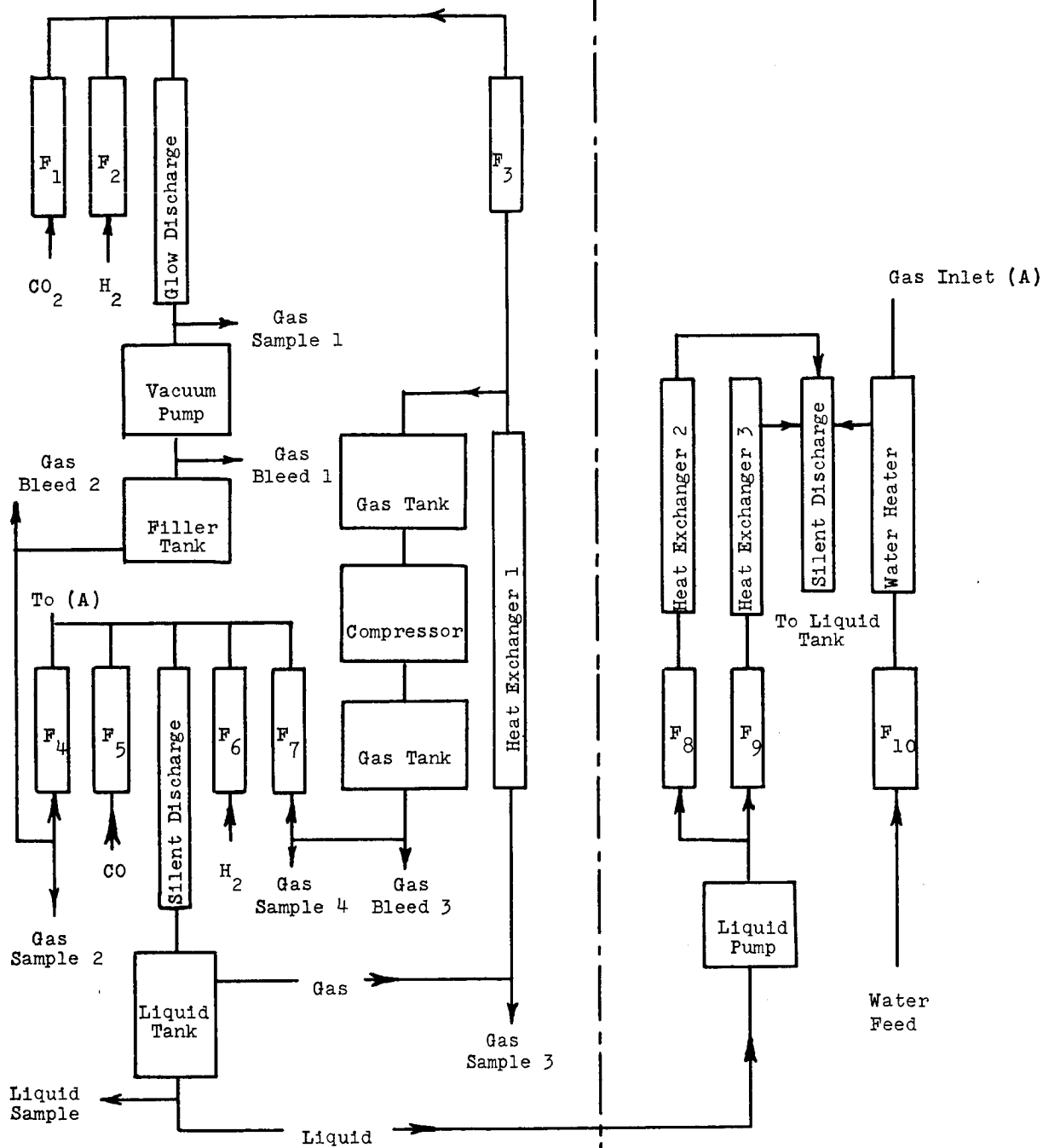


FIGURE 1. CLOSED SYSTEM FOR CONTINUOUS PRODUCTION OF FORMALDEHYDE FROM CO<sub>2</sub> AND H<sub>2</sub>

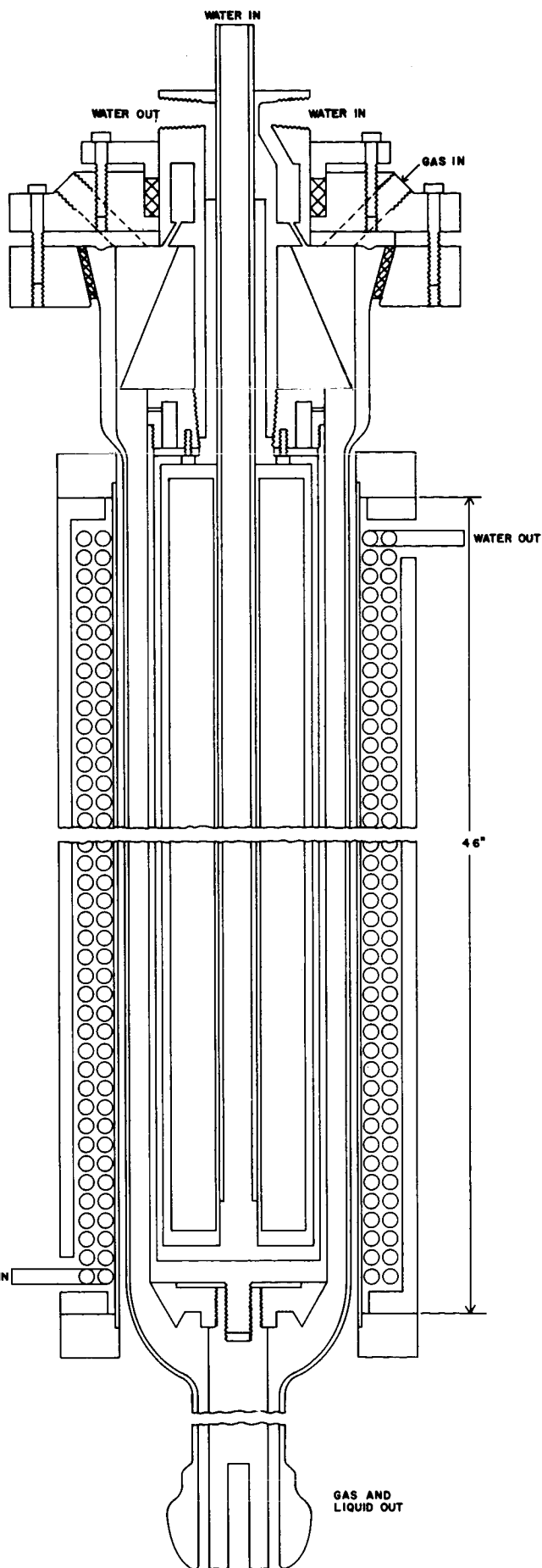
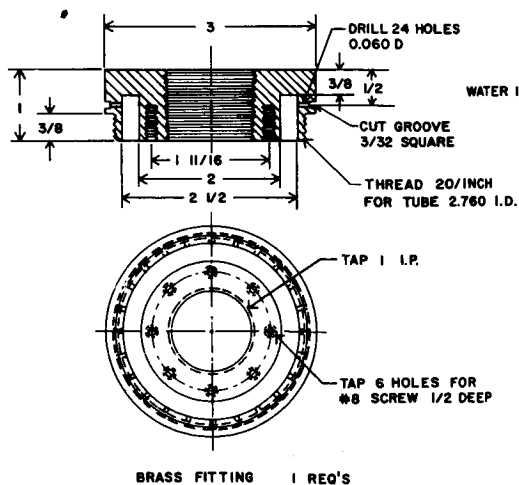
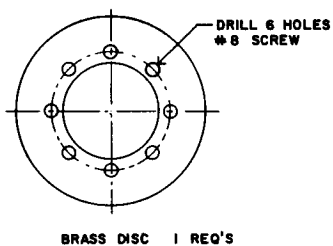
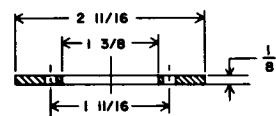
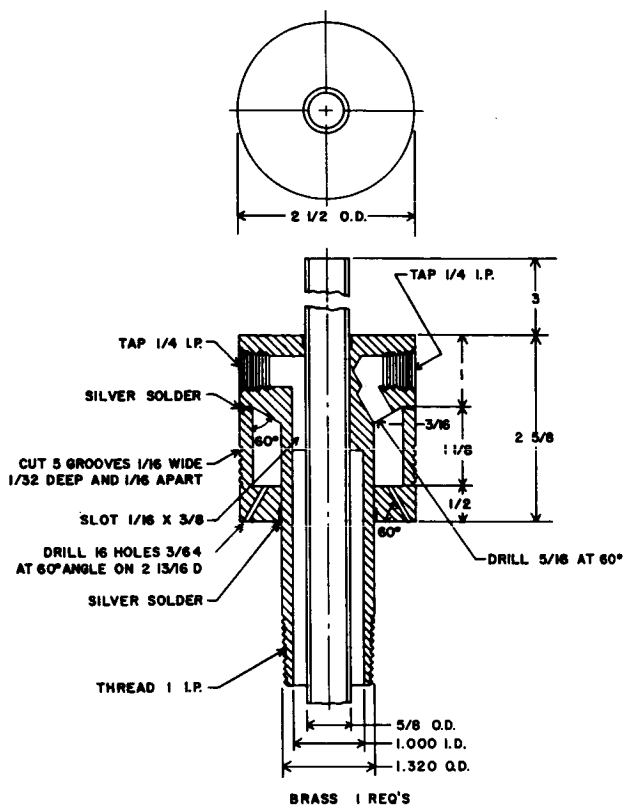


FIGURE 2  
TUBULAR REACTOR WITH  
WATER COOLED SOLENOID

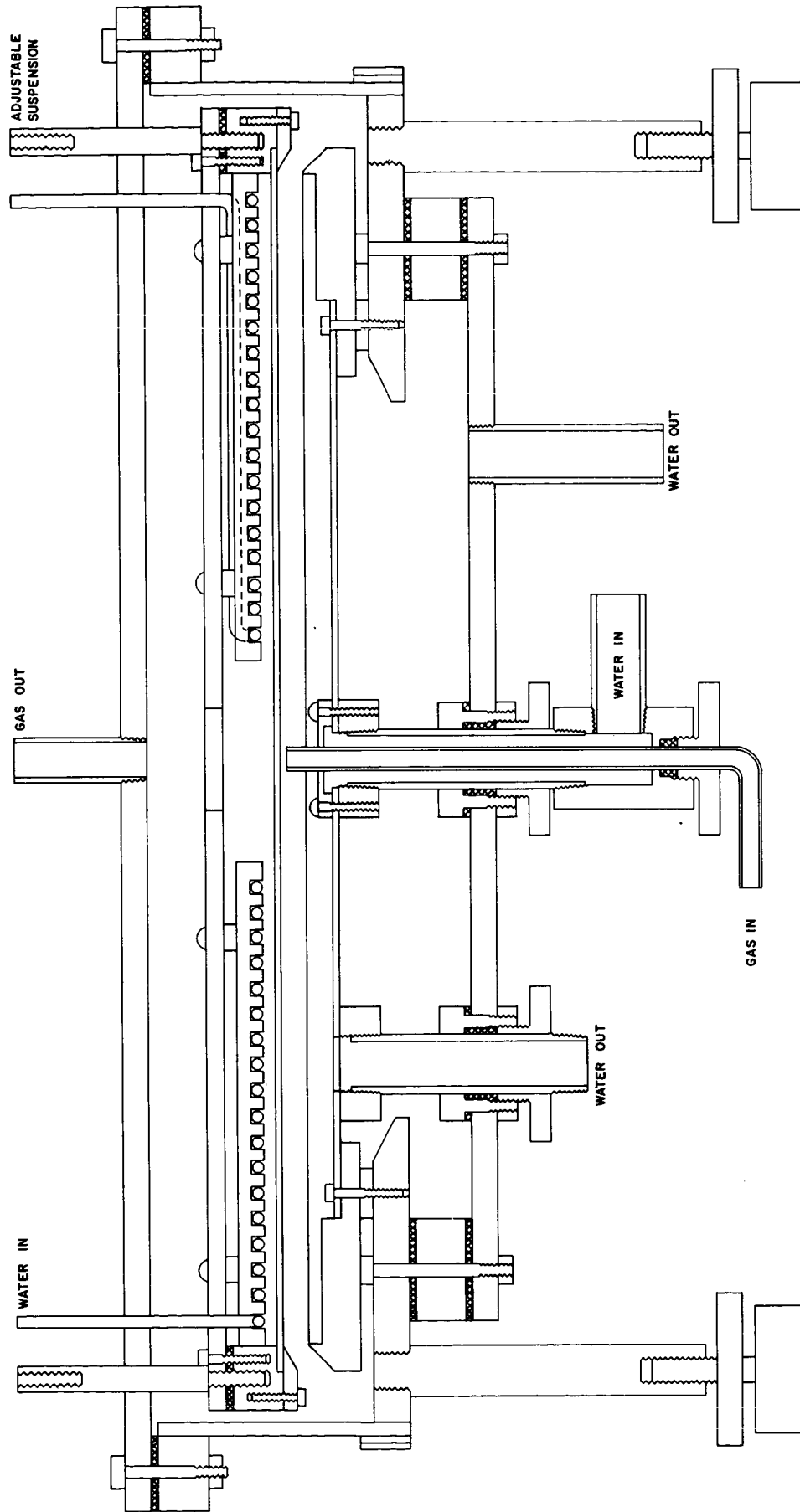


FIGURE 3 24 INCH FLAT-PLATE REACTOR

### III. The Functioning of the Flow System

Let us assume that the residence time of a gas mixture having the composition  $2\text{H}_2 + \text{CO}_2$  at a total flow of 12 lit./min. and an operating pressure of 100 mm Hg in the flow discharge is of the order of 0.15 seconds. The resulting gas stays a minimum of 15 seconds for a single pass through the tubular silent discharge reactor. If ideally complete reactions take place the residence time of the gas stream in the system would be infinite as required for true closed operation. Actually no such thing happens and allowances must be made for the degree of completion of each reaction in order to attain a closed system at steady state. Assuming that the degree of conversion of carbon dioxide attains a value of 90% and formaldehyde is formed quantitatively in a single pass the non-reacted gases must be re-cycled to the glow discharge at a rate of 1.2 lit./min. requiring only a minor adjustment of the power dissipation. The conversion of carbon monoxide to give formaldehyde appears to be a reversible reaction that tends to produce increasingly higher power yields with increasing flow rates if accompanied by the simultaneous removal of the formaldehyde present in the gas stream. To accomplish this the gas passing through the silent discharge must be re-cycled at a fairly high ratio. At some definite recycle ratio the gain attained may reach a limit. An additional fraction of the gas stream should be diverted to the glow discharge in order to attain steady state at constant pressure.

### IV. Glow Discharge Reactor, Its Mode of Operation and the Production of Graphite from Carbon Monoxide

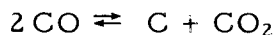
The glow discharge reactor employed was the same one used previously. To improve its performance the electrodes should be mounted at a somewhat larger distance between each other than in the case of the earlier measurements when a degree of conversion of carbon dioxide of up to 90% was attained. Simultaneously the voltage impressed should be raised strongly to allow the use of a much higher operating pressure. This in turn would permit the replacement of the vacuum pump presently used with a very much smaller and lighter one. A reduction in weight in the ratio

of thirty to one might easily be accomplished. However, although the glow discharge should be operable at pressures above atmospheric the use of a vacuum pump cannot be dispensed with since it is necessary for the initiation of the discharge.

As shown in Table 6 of Chapter 2 the degree of conversion of carbon dioxide appears to increase with pressure presumably due to the longer residence time of the gas mixture in the reactor. Data for the kinetics of the reaction taking place would allow the computation of the degree of conversion as a function of the residence time. It may also be of some interest to study the conversion of hydrogen-carbon monoxide mixtures in a glow discharge to give graphite and water. Such a process would be simple to operate and of great value during travel in space that might be extended over periods of several months. It would thus also be essential during temporary shutdown of the formaldehyde→sugar process.

The reaction  $\text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O}$  takes place under liberation of an average of 32.3 kcal/mol in the temperature range of 800 to 1800°C (JANAF Thermochemical Data 1960). At temperatures above 1000°C no catalyst is needed and the graphite formed is well crystalized.

Particularly in the presence of a catalyst carbon monoxide decomposes reversibly at moderately high temperatures (R. G. A. New and L. E. Sutton, J. Chem. Soc. 1932, p. 1415)



At equilibrium the percentage of carbon dioxide present in the gas phase is equal to 90 at 550°C but only one at 1000°C. Since further only half of the amount of carbon monoxide reacting produce free carbon and the rate of reaction rapidly decreases with the temperature this process would be of very little value.

## V. Tubular Silent Discharge Reactor

To allow greater versatility in handling operating conditions using a high gas re-cycle ratio a new reactor was built having approximately twice the inner diameter of the ones previously employed. At the same time the length of the reactor was increased by about twelve inches. Figure 2 shows a schematic diagram of the design of the new reactor and Figure 4 gives a photograph of it mounted without its magnetic shield.

The top section of the reactor was designed to allow continuous flow of water either along the inside wall of the glass mantel tube or the surface of the center electrode made of thin wall brass tubing. As a third alternative the gas stream may be moistened to carry water over a wide partial pressure and temperature range by bubbling it through a 20 inch deep column of distilled water maintained at constant temperature using a thermoregulator with a thermistor as sensing element. Two 550 watt Variac controlled cartridge heaters and a third one for off-on operation furnish sufficient power for operation over a large temperature range and at high gas flows.

To introduce an evenly dispersed stream of water along the inside wall of the mantel tube 16 small holes were drilled at an angle of 60° to the bottom face of the holder of the center electrode. Immediately below was placed a tightly held micarta cone dimensioned to allow its lower edge to come within 1/16 inch of the circular surface of the top end of the mantel tube. This section was cut from standard, flanged 4 inch Pyrex pipe. The inner diameter at the cut had previously been shrunk to that of the long tube with which it was to be joined.

To get water to flow over the surface of the center electrode its top closing disc was threaded to screw into the brass tube and a shallow groove cut in its periphery. In the center of this groove a number of small, evenly spaced holes were drilled to connect with an inner deep groove, which could be covered with a thin brass plate to stop water from flowing out. The inner, free volume of the center electrode is relatively large and in order to decrease the amount of liquid required for operation of the system a closed insert with a volume of about 3700 cc was provided. The insert was centered around the water inlet tube.

The liquid flowing out of the reactor drains into a welded stainless steel tank from which it may be re-circulated using an insulated pump. The stream is divided up between two flowmeters and before re-entering the reactor the parts are given definite temperatures in the two glass heat exchangers each provided with linear coils containing 45 feet of glass tubing.

#### VI. The Solenoid for the Tubular Reactor

The solenoid previously employed for the study of the effect of a magnetic field on the yield of formaldehyde consumed about 2500 watts at a current of only 20 amperes. The strong temperature rise accompanying this higher power dissipation made longer runs impossible. The new reactor has been provided with a tubular solenoid having a resistance of 0.25 ohms. At a current of 100 amperes the power consumed is about equal to that of the first solenoid but at a water flow of 3000 cc per minute the temperature rise at the water exit end would be about 24°C. The coil will be enclosed in a split steel tube which should more than double the intensity of the internal magnetic field.

The question of the future usefulness of a magnetic field to increase the yield of formaldehyde probably is debatable. A superconducting solenoid may be built to produce extremely strong fields of the order of 20 kilogauss or higher without consumption of additional power. With higher adequate thermal insulation now available it is possible to use it for operations at ordinary or even higher temperatures as ascertained during a recent visit to Westinghouse in Pittsburgh. The weight of the helium liquifier and the amount of power required for its operation may however eliminate any advantage gained. It should nevertheless be pointed out that the kinetics of reactions in electric discharges with superimposed magnetic fields as yet is practically unknown.

## VII. Flat Plate Reactor

The yield of product derived from a chemical reaction taking place in an electric discharge is dependent on size and design of the reactor employed. It therefore was regarded as essential that the reactor employed to obtain the data necessary to design those to be built for future adaptation to a closed respiratory system with regard to size would come within a factor of one half or one third of that of the latter. The new flat plate reactor has an active surface area about 2.5 times larger than that of the first one built and has been improved considerably with respect to a number of details.

The method of suspending the glass plate has not been changed but the cooling coil spiral above it was lifted up from the surface of the glass to avoid accidental impacts or stresses that might cause it to break. A strong mounting of the coil was obtained by soldering it to eight radial supports slotted at half inch intervals to the same depth and width as the diameter of the tubing employed. The supports were each anchored at two points to a 3/8 plexiglas disc covering the top edge of the one inch high micarta ring, to the bottom of which the glass plate was sealed with an epoxy resin.

Although this is not shown in the schematic diagram of the reactor given in Figure 3 the water in and outlets for the cooling coil and the four height adjustment rods for the plate glass assembly were all provided with packing glands to avoid gas leakage. The circular wall enclosing the top section of the reactor was made of a double 1/8" thick sheet of annealed Plexiglas premolded to its outer diameter. The bottom part of the Plexiglas sheet was held in place tightly by a double ring of cold rolled steel and finally sealed both inside and outside to the supporting micarta disc using an epoxy resin. The top outer micarta ring also was sealed to the Plexiglas sheet in a similar manner.

The adjustment of the distance between the underside of the glass plate and the surface of the liquid flowing out below was accomplished using the small turrets designed for the purpose and shown on the top of the reactor in Figure 5. The plate assembly was lifted with



screws held by these turrets. The screws could be adjusted with a precision of about 0.001<sup>in</sup> using inserted gage blocks. This method allowed re-tightening of the packing glands without disturbing either the height or the tilt of the glass plate. The maximum distance that could be provided between the plate and the surface of the liquid was about one inch which gives an ample range for the study of the effect of variations in diameter of the annular space as applied to a spinning, tapered tubular reactor with continuously flowing liquid phase.

#### VIII. Power Supplies and Other Instrumentation

No changes have been made in the power supplies employed for either the glow or the silent discharge reactors, except that in the case of the latter, a larger high frequency-high voltage transformer was acquired and a DC power supply was built for a second generator with the same characteristics as the one used so far and to be run in parallel.

It should be pointed out that at frequencies above 3000 c.p.s. a square wave generator built using solid state components would be far more efficient and very much lighter than the type of mechanical, sine wave generator employed so far. The transformer required for current with square wave form to give sufficiently high voltage for operation of the silent discharge may however be somewhat of a problem.

All instrumentation in the form of flowmeters, manometers, electrical meters, variable transformers and all switches have been assembled on two micarta panels as shown in Figures 6 and 7. The entire set up has been leak tested and is in good operation condition.

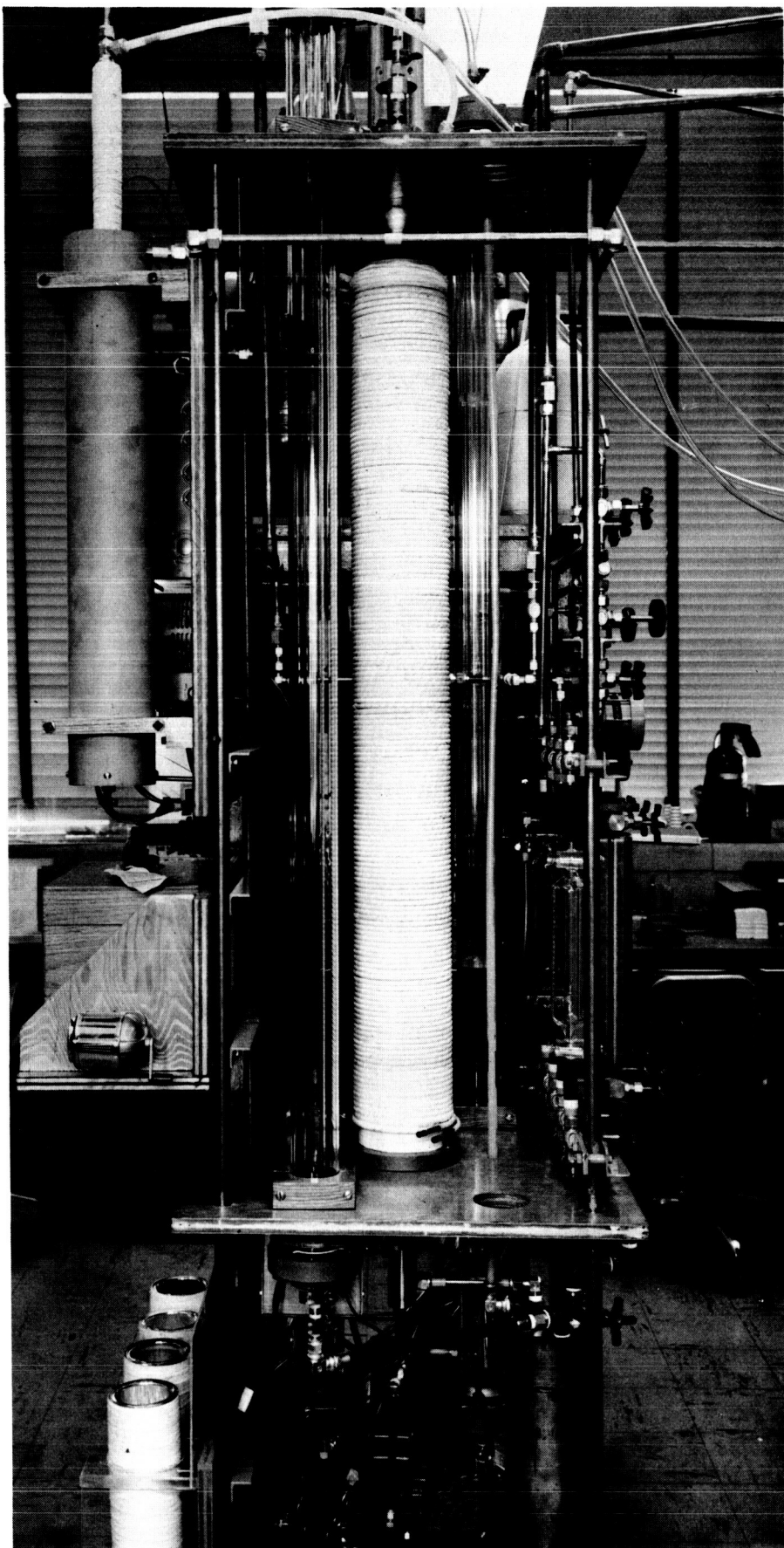


FIGURE 4. Tubular Reactor with Solenoid

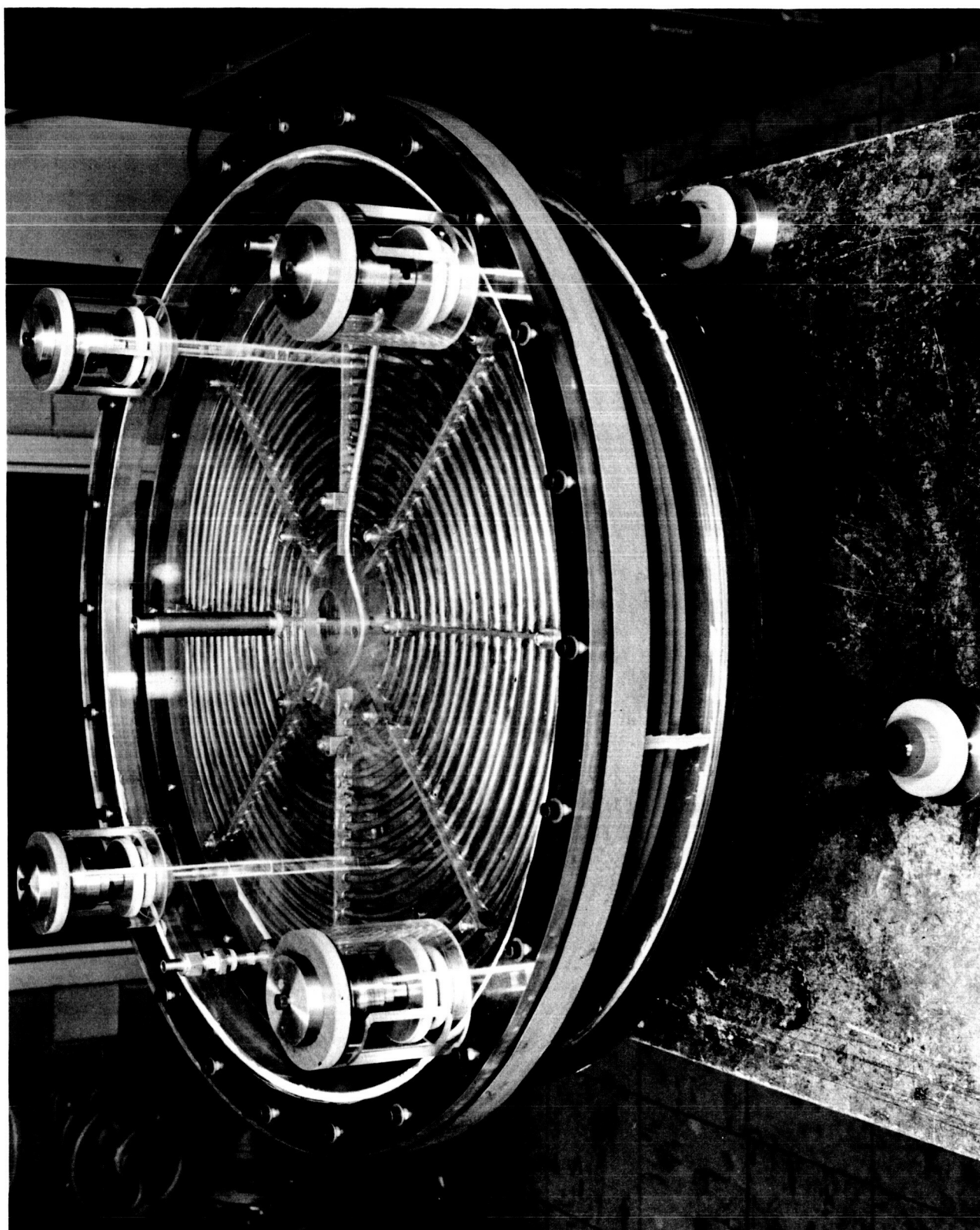


FIGURE 5. Photograph of Flat Plate Reactor

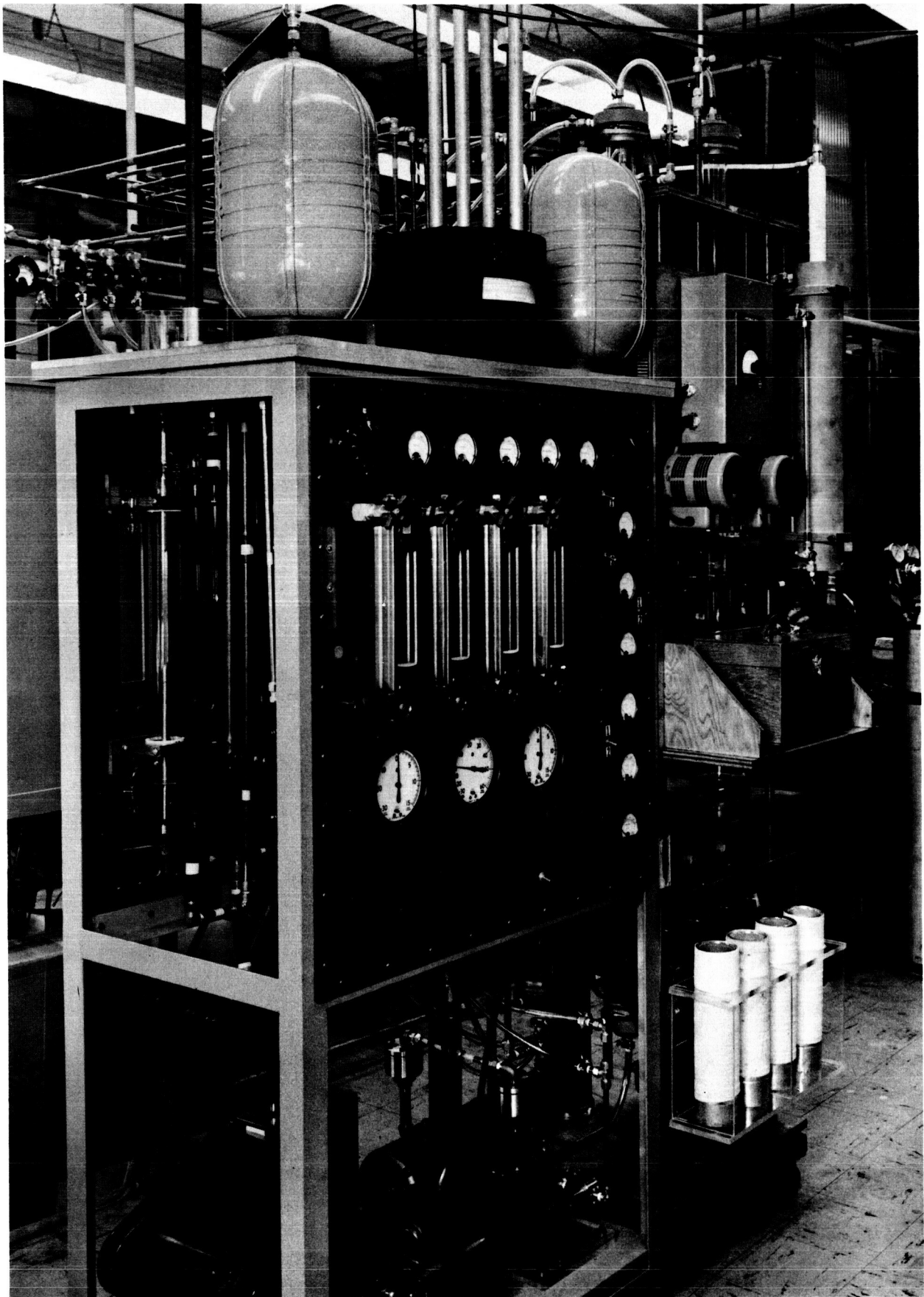


FIGURE 6. Photograph of Front Panel Assembly



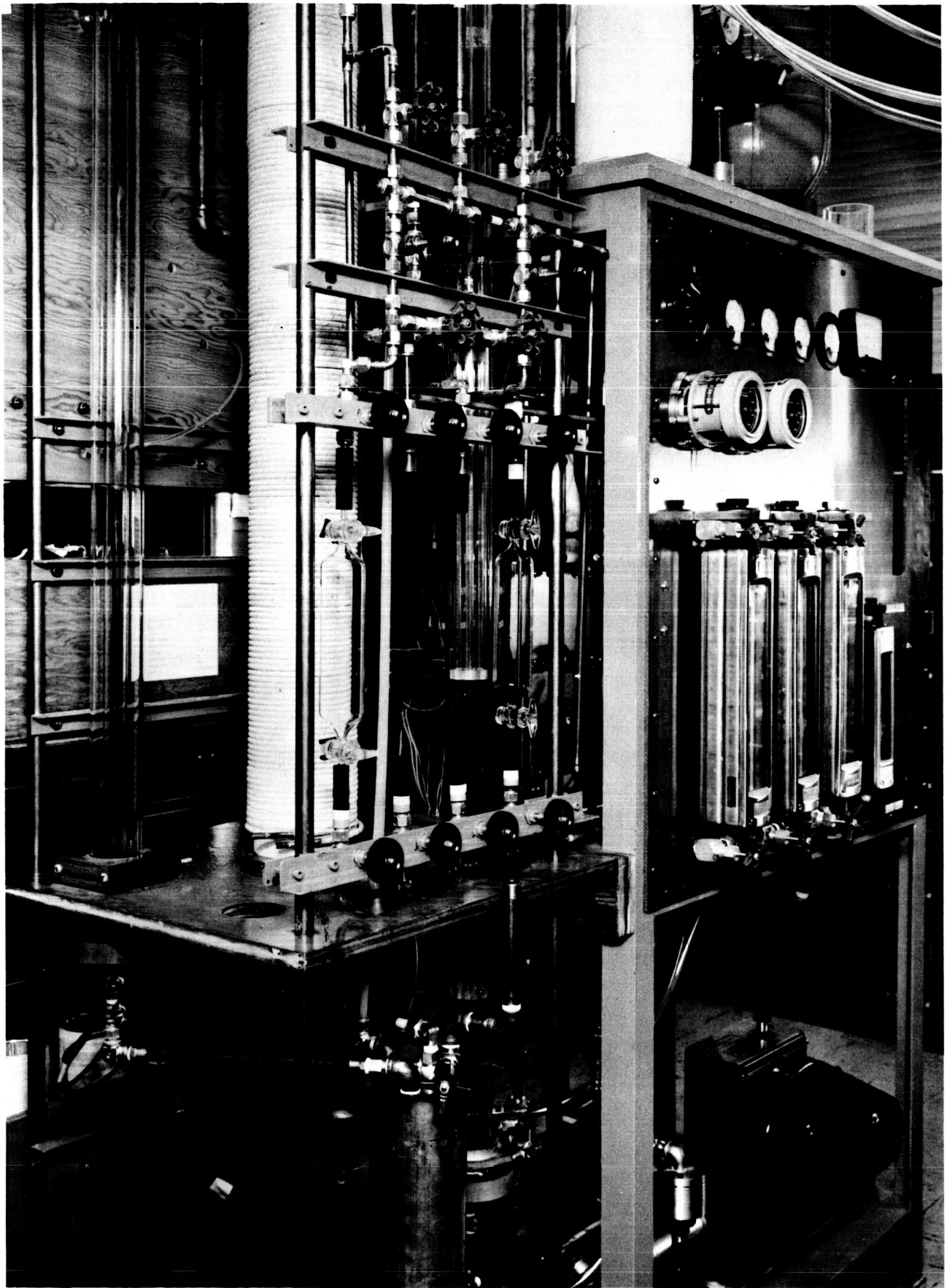


FIGURE 7. Photograph of Back Panel Assembly

## IX. Principles for Work Program

The reason for studying the behavior of both a tubular and a flat plate reactor is connected with the design visualized for a reactor operating at weightlessness. The latter generates its own gravitational field by the use of a spinning, tapered mantle tube as described in Chapter 3. In so doing a liquid fed in at the small end will flow out to produce a film of uniform thickness as determined by the kinematic viscosity of the liquid, the angular velocity, degree of taper and diameter of the reactor mantle tube. As long as free flow of the liquid is attained the actual thickness of the liquid layer is probably immaterial since absorption of the formaldehyde produced takes place only at its surface. However, this allows a large degree of freedom in choice of reactor parameters and angular velocity.

The yield of formaldehyde in the case of the two types of reactors completed is affected by the following variables:

- |                      |  |
|----------------------|--|
| 1. power factor      | 6. diam. of annular space                  |
| 2. power input       | 7. temperature                             |
| 3. current frequency | 8. pressure                                |
| 4. current waveform  | 9. gas flow rate                           |
| 5. magnetic field    | 10. CH <sub>2</sub> O conc.in liquid phase |

The effect of most of these variables may be studied using either type of reactor. However, the flat plate reactor does not lend itself to the study of the effects of temperature and pressure variations and that of an impressed magnetic field. The effect of changes in gas re-cycle ratio cannot be studied directly in a completely closed system due to the steadily increasing pressure of non-reacted gas. To attain sufficiently high rate of formation of formaldehyde in a closed system, this should be considered as a limiting case that will require close control of all operating variables.

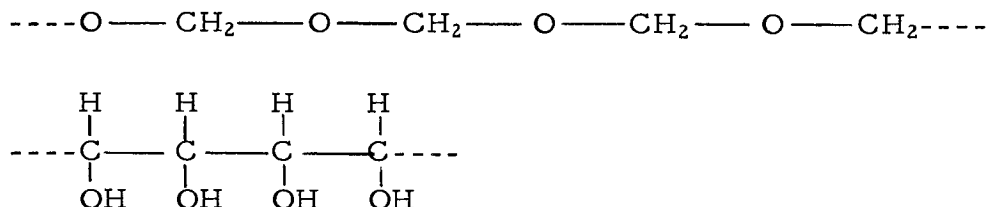
PART II  
THE PREPARATION AND EVALUATION OF  
SUGARS FROM FORMALDEHYDE

by P. W. Mitchell

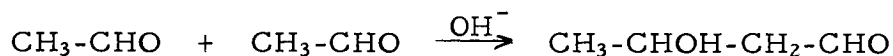
## CHAPTER 5. THE CONDENSATION OF FORMALDEHYDE TO SUGARS

### I. Literature Review

Formaldehyde is a highly reactive chemical and polymerization is one of its more characteristic properties. Two fundamentally different polymer types are theoretically possible as shown below:



Polymers of the first type are known as polyoxymethylenes and are reversible, that is, they behave chemically as formaldehyde. Polymers of the second type are irreversible and comprise oxy-aldehyde and oxy-ketones, the largest members being of six carbon atoms in length. In this last named group belong the hexose sugars. The formation of a carbon to carbon polymer is more correctly described as a condensation reaction and it bears a resemblance to the well-known aldol reaction of aldehydes (1, 2, 3). There is, however, a difference in that formaldehyde contains no methylene group and aldol condensations usually end when two aldehyde molecules have reacted as illustrated below:



In aqueous formaldehyde, the reaction is favored by alkaline agents, but with anhydrous solutions in alcohols, glycols or glycerol it can apparently also be carried out in the presence of weak organic acids (4). In addition, it is induced by U. V. light and there is evidence that it is involved in the mechanism of photosynthesis (5, 6, 7, 8, 9, 10). It also has been claimed that formaldehyde can be formed from CO<sub>2</sub> and

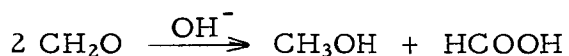


H<sub>2</sub>O (6, 11, 12). Although sugars are the predominant product when this condensation is allowed to proceed to completion, glycolic aldehyde has been isolated and is apparently the first produce (13):



Other products demonstrated (13, 14) include glyceraldehyde (CH<sub>2</sub>OH-CHOH-CHO), dihydroxyacetone (CH<sub>2</sub>OH-CO-CH<sub>2</sub>OH) and erythrose (CH<sub>2</sub>OH-CHOH-CHOH-CHO).

In the presence of alkalies, formaldehyde also undergoes the Cannizzaro reaction:



This occurs especially with strong alkalies such as sodium and potassium hydroxide (15, 16, 17, 18, 19, 20, 21, 22, 23, 24). In addition di- and tri-oxybutyric acids may be formed (25). The mechanism of the Cannizzaro reaction with regard to the influence of the catalyst has been studied by Pfeil (26), Pfeil and Paul (27) who found it to be bimolecular with an excess of alkali, and Pajunen (28) reported it to be trimolecular in dilute equimolecular solutions with a heat of activation of 22.3 kcal. The reaction is accelerated by copper (30), Raney nickel (31, 32), acetone (33) and by other ketones (34). The presence of cupric oxide results in the liberation of hydrogen but pure cuprous oxide has no effect (35, 36). Losses of formaldehyde via the Cannizzaro reaction will have to be kept to a minimum in the sugar synthesis.

It was Butlerow (37) who, in 1861, first observed the formation of sugar-like substances from formaldehyde and he called the crude product "methylenitan". By careful handling of the product which decomposes to brown tarry materials when heated in the presence of alkalis, Loew (9) succeeded in isolating a sweet syrup which reduced Fehling's solution but was optically inactive. From this syrup Loew (9, 10, 15) obtained an approximately 75% yield of a mixture of hexose sugars (formose) possessing the empirical formula C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>. An

osazone isolated from formose was demonstrated to be phenylacrosazone which is a derivative of inactive DL-fructose (alpha acrose). A typical procedure for the preparation of formose involved the agitation of approximately 4% aqueous formaldehyde with an excess of calcium hydroxide for 30 minutes, followed by filtration and allowing the solution to stand for 5 or 6 days. Calcium ions were removed by treatment of the solution with oxalic acid and evaporation gave the crude syrup. Loew's work indicated that the condensation proceeded best under the influence of alkaline earth hydroxides and the hydroxides of weakly basic metals such as lead and tin and it was accompanied by a comparatively long induction period.

Formose also contains a sugar with a branched chain (10, 38, 39) and a ketopentose  $C_5H_{10}O_5$  (40). Euler (41) and Loew (42) showed that refluxing of 2% aqueous formaldehyde with calcium carbonate gave as the main product, DL-arabinoketose,  $(CH_2OH-CHOH-CHOH-CO-CH_2OH)$ . When the reaction was stopped before completion, glycolic aldehyde and dihydroxyacetone were identified among the products. The product "methyl-enitan" described by Butlerow is obtained by heating polyoxymethylene with lime water and also by heating aqueous formaldehyde with baryta water at 55° to 60°. It appears to be mainly decomposition products of the sugar mixture initially formed (20, 21, 37, 43, 44). Seyewetz and Gibello (45) have described the preparation of a condensate which must consist largely of glyceraldehyde and dihydroxyacetone, by heating polyoxymethylene with sodium sulphite solution. Loew (10, 46) has shown that sugars can be formed by heating dilute formaldehyde with lead, the latter being converted in part into lead hydroxide. If the condensation was carried out with granulated lead at about 60°C with the addition of some magnesia and magnesium sulphate, a sugar mixture was obtained in which a substantial amount of a normal hexose was present (10, 39, 47). The action of granulated tin (9, 46) was probably due to its lead content.

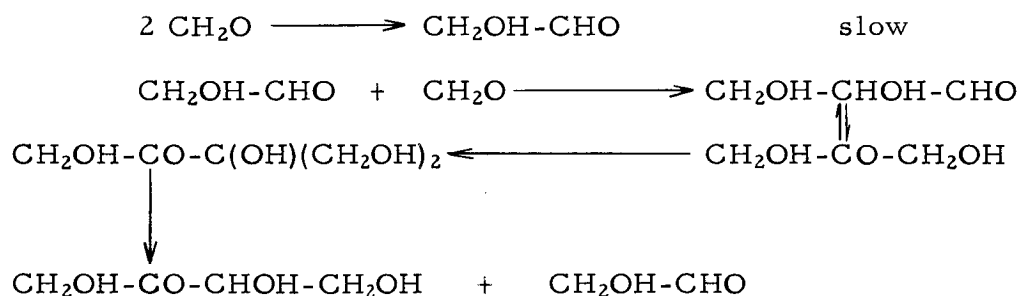
Prolonged heating of formaldehyde with zinc carbonate (25) gave sugary products together with dihydroxyacetone, polyhydroxy acids and acetoin, the latter being supposed to derive from the decomposition of the sugars. Also formed were quantities of methanol and formic acid

by the Cannizzaro reaction and this seemed to predominate when formaldehyde was heated with zinc dust or with reduced iron (48). Franzen and Hauck (50, 51) have produced evidence for the formation of salts between formaldehyde and the hydroxides of Cu, Ca, Sr, Mg, Zn, Cd and Pb.

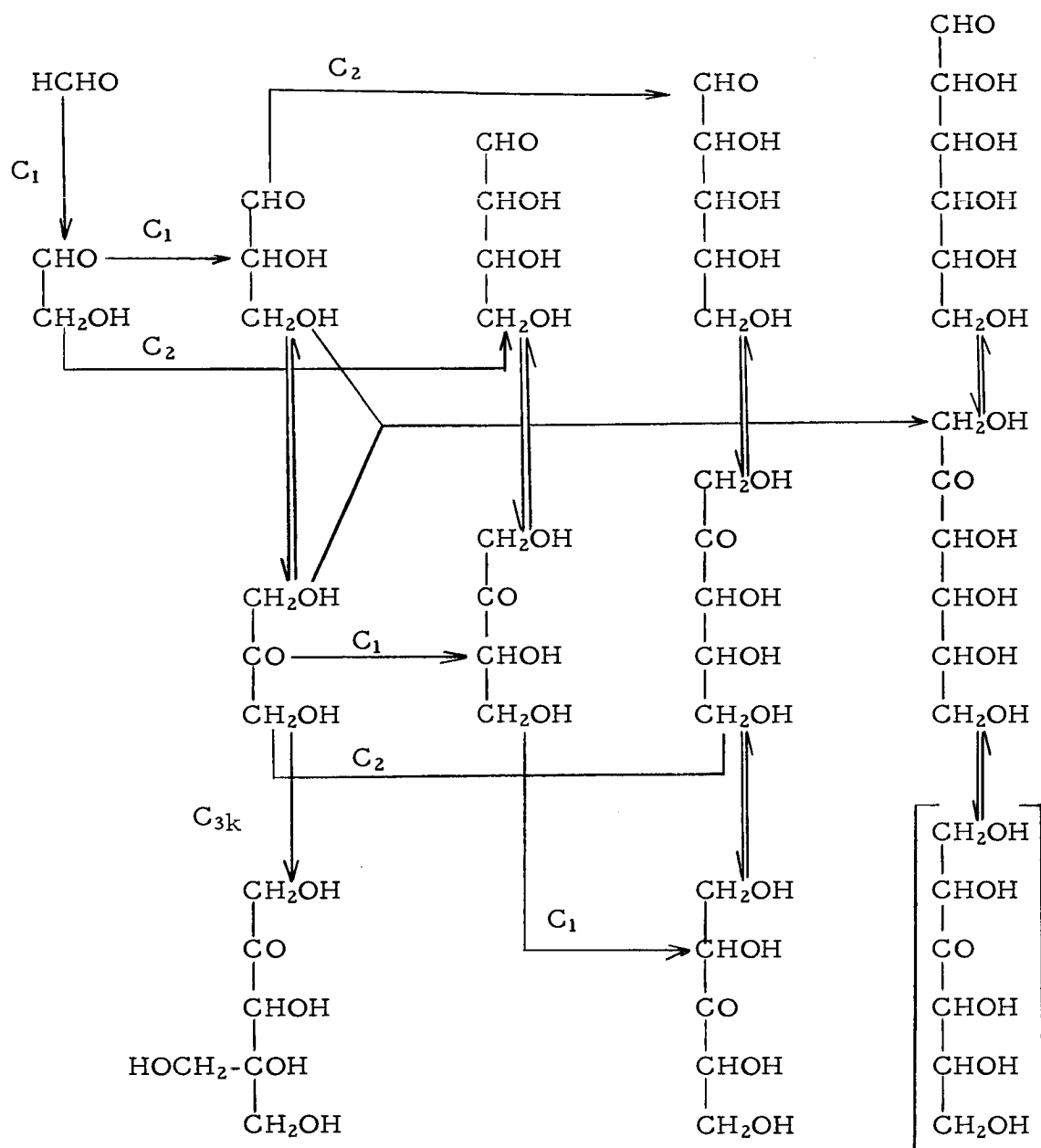
Further work on the condensation of formaldehyde by alkaline lead oxide and magnesium sulphate at 50° to 60°C or by calcium carbonate, calcium phosphate or lead hydroxide at boiling temperature has shown the products to contain DL-fructose, DL-sorbose and DL-araboketose (52, 53, 54). Schmalfuss (55, 56) using magnesia in reactions under pressure obtained methanol, formic acid, diacetyl, dihydroxyacetone and a mixture of sugars in quantities varying with the conditions used. The last named author also used magnesia under conditions described by Vogel (57) and showed that the reaction was accelerated by the addition of glucose, fructose, dihydroxyacetone, magnesium chloride, magnesium formate or magnesium acetate and stopped by copper formate or acids. Ewart (58) and Salkowski (59) found that by comparison with calcium, barium, strontium or magnesium hydroxides, the alkali carbonates and bicarbonates gave only poor yields of sugars. The formation of "formose" using sodium carbonate is accelerated by traces of D-glucose, and Kingsbury (60) made this fact the basis for a method of estimation of D-glucose in biological fluids. Ewart (61) also studied the effect of the carbonates of calcium, magnesium, barium and strontium and has published some results on the preparation of formose using dilute caustic soda (58, 62). It is interesting to note that sunlight in the presence of magnesium, zinc, their oxides or their carbonates will convert dilute formaldehyde into a sugar mixture together with a small quantity of methanol (63, 64).

In more recent years, interest has been maintained in the condensation of formaldehyde to sugars. The literature on the influence of alkaline earths has been reviewed by Triem and Schwab (65) and Adickes and DuMont (66). Pfeil and coworkers (67) have carried out new work on the catalytic effect of different metals and have proposed a mechanism

for the reaction. It seems to be established that in the first stage of the autocatalytic reaction, glycolic aldehyde, dihydroxyacetone and tetroses develop. For example, after heating 1 liter of 4% formaldehyde with 5 g. of lead hydroxide for 1/2 hour and hydrogenating the products, glycol, glycerine, threose and some erythrose were obtained (68, 69). Some Russian workers (70) have isolated glycolic aldehyde by reacting formaldehyde with calcium hydroxide in the presence of glucose. The kinetics and the mechanism of the sugar formation have been studied by Balezin (71). Kusin compared the action of calcium hydroxide with sodium hydroxide (72) and studied also the effect of basic calcium salts of organic acids (73). He demonstrated too the acceleration of the condensation in the presence of calcium hydroxide or lead oxide by glycerine, glycol, and glycollic aldehyde, the last named substance being studied in comparison with different sugars (74). Benzoin has also been shown to be an accelerator (75, 76) in addition to acetoin (76), benzoyl carbinol and analogs (77), and ascorbic acid (78). Nitro compounds are said to have a retarding effect (77). It is interesting to note that Katzschnmann (79) has proposed a series of reactions involving a reactive intermediate which he has isolated and identified. The possible mechanism is given as follows:



Pfeil and Ruckert (80) in their detailed investigation of the sugar forming reaction make no mention of this mechanism but do refer to some other recent ideas (81, 82) with which they are in disagreement and propose the following rather simple scheme:

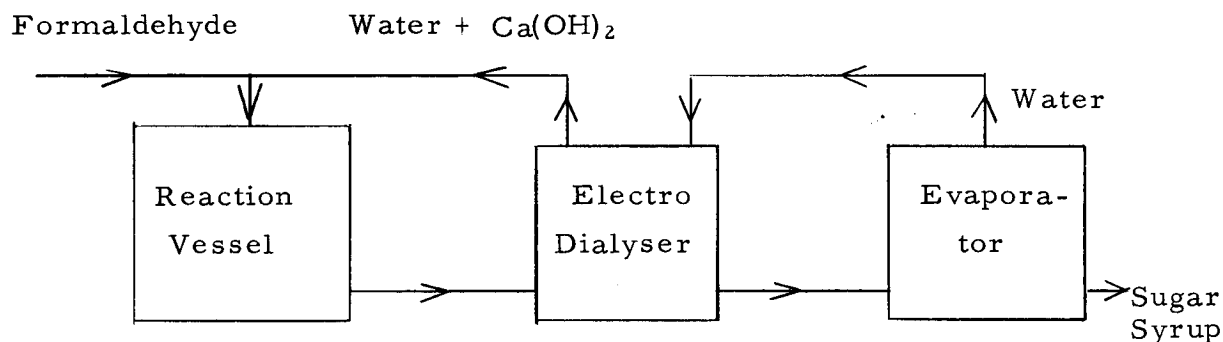


Balezin claims that the role of calcium hydroxide in the condensation is not only to give the necessary alkalinity, but also as an essential component of an intermediate complex formed in the condensation process (83).

It is clear from an appraisal of the work that has been done on this extremely interesting reaction that the theoretical aspects have yet to be

put on a satisfactory basis. However, from a practical point of view, one can work in the general direction of:

- (a) Minimizing losses of formaldehyde due to the Cannizzaro reaction.
- (b) Variation of the reaction conditions to give the maximum yield of sugars. This involves care to avoid loss of sugars by their well-known degradation in the presence of alkali.
- (c) An attempt to introduce an element of stereospecificity into the reactions so that only the more useful (nutritionally) sugars predominate.
- (d) The choice of experimental conditions which will ultimately lend themselves most readily to a continuously operating process. This will probably possess the features shown in the following diagram:



## II. Experimental

Some work has been carried out on a preliminary basis to gain familiarity with the condensation reaction and to enable a systematic plan of approach to be developed.

The exothermic nature of the condensation reaction of 4% aqueous formaldehyde at 100°C in the presence of excess calcium hydroxide was confirmed. The completion of the reaction was shown by complete disappearance of the odor of formaldehyde and the production of a yellow to

brown color; when the condensation was carried out at 60°C and the amount of calcium hydroxide reduced, little or no reaction occurred, the optimum amount was found to be approximately 1 mol. of calcium hydroxide for 10 mols of formaldehyde or 23% calcium hydroxide by weight. Under these conditions, the reaction was complete in about 1/2 hour, giving a clear yellow colored solution. It was noted that addition of a small amount of alumina completely stopped the reaction.

A preliminary isolation of the condensate was achieved by evaporation of the solution, after neutralization with formic acid, to small volume followed by precipitation of inorganic material with absolute alcohol. This was separated by filtration, and further evaporation of the filtrate gave a sweet tasting solid, which, however, still contained inorganic material. An improved method of purifying the product was achieved by the use of a mixed bed ion exchange column. The reaction solution was passed through a column containing about 200 ml. of resin for 10 g. of formaldehyde and this gave a completely deionized effluat. This, on evaporation, yielded a pale yellow sweet tasting syrup in a yield of 55% by weight of the formaldehyde used. Exhaustive washing of the column with water gave no more material and it must be assumed that the loss was due to conversion of formaldehyde in part to formate by the Cannizzaro reaction and to degradation of the sugars initially formed, to acids in the presence of alkali. That the latter occurs is well known and has been confirmed by comparative experiments with D-glucose, about 40% of it being converted into acidic products by treatment with lime under conditions comparable with the formaldehyde reactions.

With a view to having a quick nutritional test procedure, the action of yeast on the condensate obtained from the ion exchange column has been examined. This particular material appears to contain no yeast fermentable material. It has been found that the crude reaction solution after neutralization with sulphuric acid may be used directly for fermentation studies, thus obviating the necessity for deionization and evaporation. The titration value provides a useful indication of the amount of organic acid formed during the reaction.

For the production of salt free material to use in animal feeding tests, the use of electrodialysis will be examined and the composition of the condensates is going to be studied by means of cellulose chromatography.

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## CHAPTER 6. THE CONTINUOUS PREPARATION OF SUGARS

### I. Evaluation of Sugar Syrups, Effect of Catalysts and Continuous Preparation of Sugars

The sugar syrup described in the previous chapter was examined at the Food and Drug Research Laboratories as a carbon source for yeast growth. It was found to have an activity equivalent to about 5% of its weight of D-glucose. Paper chromatography of the syrup showed that it contained dihydroxyacetone, glyceraldehyde and pentoses but gave no evidence of hexoses. The osazone mixture prepared from the syrup contained at least six distinct compounds.

Both ethanol and methanol were found to be unsuitable solvents for the condensation reaction. Considerable dilution with water was required before any reaction took place. The formation of sugars was, however, accelerated in aqueous solution as reported in the literature, by the presence of small amounts of methanol. The catalytic effect of various sugars and of dihydroxyacetone was also confirmed (Table 1). The point of sugar formation was taken as the point at which the solutions became yellow.

Table 1. Catalysts for the Condensation of Formaldehyde to Sugars

<u>Compound</u>	<u>Molar Ratio Catalyst: HCHO</u>	<u>Reaction Time (min.)</u>	<u>Percent reduction in time</u>
Acetoin	1:66	8.2	57
Dihydroxyacetone	1:68	3.25	72
D-L-Glycer- aldehyde	1:68	4.1	78
D-Fructose	1:136	6.0	68
D-Glucose	1:136	6.5	66
D-Ribose	1:113	7.1	63
No catalyst	-	19	-

No sugar producing reaction occurred when formaldehyde was heated with tetramethylammonium hydroxide (a strong base), but reaction took place with the addition of calcium chloride. This experiment and others described below, illustrate the importance of calcium ions in the reaction. These are sequestered to some extent by formaldehyde. Thus, calcium chloride in an aqueous solution of formaldehyde required a 145 percent excess of standard alkali to cause precipitation of calcium hydroxide. The amount of alkali required to cause the formation of sugars when the above solution of calcium chloride and formaldehyde was heated, corresponded to the production (in solution) of the minimum amount of calcium hydroxide found necessary in earlier experiments. When sequestering agents such as ethylenediamine tetraacetic acid (EDTA) or "Dowex" chelating resin were added, no sugar forming reaction took place. Thus a strongly alkaline solution of formaldehyde, calcium chloride and EDTA could be refluxed for 3.5 hours without reaction occurring. In the absence of EDTA, reaction took place in 30 seconds.

The effect of varying amounts of calcium hydroxide on a 4.5 percent solution of formaldehyde was studied. Aliquot samples of the reaction solution were withdrawn at intervals of five minutes and titrated against standard acid. Each neutralized aliquot was deionized by passage through a column of mixed bed resin, concentrated and analyzed by paper chromatography. The results are shown in Figure 1 and in Table 2.

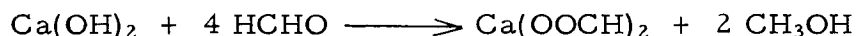
Table 2. Time of Color Formation During Sugar Formation Using 0.3 mole of Formaldehyde in 200 ml. of Water at 60°C

	Conc. of $\text{Ca}(\text{OH})_2(\text{a})$ (moles in 200 ml.)	Reaction time * (t)	Moles of $\text{Ca}(\text{OH})_2$ used at t.	a x t
I	0.067	17 min.	0.023	1.14
II	0.044	24.2	0.026	1.06
III	0.033	26.25	0.023	0.87
IV	0.027	48	0.024	1.29
V	0.021	-	-	-

\* Time of color formation, see Figure 1

The appearance of sugars occurred sharply after an initial induction period and coincided, except for experiment IV, with the appearance of a yellow reaction solution. This point is marked "X" on the curves in Figure 1. As seen in Table 2, there is a rough correlation between the time of the sugar reaction and the initial amount of calcium hydroxide used. At point of color formation, little or no formaldehyde remains and so the continued consumption of alkali must be due to the formation of acidic products by degradation of the sugars (1, 2, 3, 4). Figure 2 shows the consumption of alkali when an aqueous solution of D-glucose was heated with calcium hydroxide. A deep yellow color was obtained immediately on addition of the alkali.

The amount of calcium hydroxide neutralized at the point of color formation in each experiment was approximately the same. It was thought that this might represent catalysis of the reaction when a certain minimum amount of methanol had been formed from the reaction:



This, however, was not the case since the presence of methanol in the reaction mixture reduced the reaction time by only 10 minutes. By comparison, D-glucose was a much more effective catalyst and even cellulose powder had an intermediate influence (Table 3).

Table 3. Catalysts for the Condensation of Formaldehyde to Sugars  
0.3 mole of Formaldehyde in Water (200 ml.) containing 0.027 mole of  $\text{Ca(OH)}_2$  at 60°C

Catalyst	Amount Added	Reaction Time (min.)	Moles $\text{Ca(OH)}_2$ Used
1. Methanol	0.125 moles	38	0.020
2. D-glucose	0.0028	7	0.010
3. Cellulose*	0.0112	15.5	0.017
4. Cellulose*	0.112	10.75	-
5. Reaction Solution**	25 ml.	6.75	-
6. Reaction Solution	10 ml.	7.3	-
7. Reaction Solution	5 ml.	9.75	0.012

\* Heterogeneous Catalysis

\*\* Taken from an uncatalyzed experiment, after 48 minutes, using 0.024 moles of  $\text{Ca(OH)}_2$

In the catalyzed reactions, less alkali was neutralized, that is, loss of formaldehyde by side reaction to give formic acid (and methanol) was reduced and hence a greater yield of sugars was made possible. The obvious choice of catalyst was the reaction solution itself and this was found to be very effective (Table 3, Experiments 5, 6 & 7).

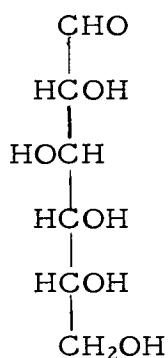
The reaction mixture used in Experiment 6 of Table 3 was chosen for use in an apparatus designed to operate on a continuous basis. This consisted of a coil 5 meters in length of "Tygon" tubing having an inside diameter of 3 mm. and an inside volume of 34 ml. The coil was immersed in a water bath maintained at 60°C and the suspension of calcium hydroxide in 4.5 percent aqueous formaldehyde containing catalyst was pumped through at a rate of 4 ml./min. giving a reaction time of 8.5 minutes. The clear yellow solution leaving the coil was cooled, treated with carbon dioxide to precipitate calcium ions (except those combined with acid radicals) and then deionized by passage through a column of mixed bed ion exchange resins. The effluent which had a conductivity equivalent to less than 5 parts per million of sodium chloride, was then concentrated in a flash evaporator at 50°C and 15 mm. pressure. The apparatus is illustrated in Figure 3.

A syrup (637g) containing 7.7 percent of water was obtained using this apparatus, from 855 g. of formaldehyde, 212 g. of calcium hydroxide and 19 liters of water. The yield of anhydrous material allowing for solution losses during the run was 655 g. or 77 percent of the formaldehyde used. No formaldehyde was detected in the optically inactive syrup. It reduced Fehling's solution being equivalent in this respect, to about one-third its weight of glucose. The syrup was sweet tasting with a very slight bitter after effect due possibly to the presence of traces of formic or saccharinic acids. The acid content was found to be 0.0026 equivalents per 100 g.

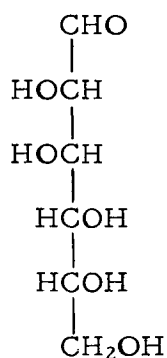
Paper chromatography of the syrup showed clear evidence of hexoses. Pentoses and some glyceraldehyde and dihydroxyacetone were also present. The slowest moving material had an  $R_F$  value very close to that of glucose and this slowest moving material was found by cellulose column chromatography to constitute about half the mixture. Its identity has not yet been established.

By contrast with the material prepared in the batch process, this new sugar mixture, as a 10 percent aqueous solution (containing phosphate), was readily fermentable by Baker's yeast. A 2.2 percent solution of ethanol was obtained. The pentoses were still present but the hexoses were markedly reduced. The Food and Drug Research Laboratories have confirmed in a preliminary report that for yeast, the sample is equivalent in activity to about 25 percent its weight of D-glucose.

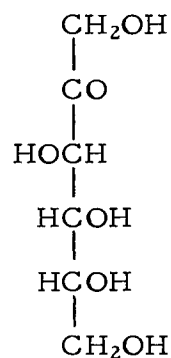
Only sucrose (a compound of D-glucose and D-fructose) and the D-forms of glucose, mannose and fructose are fermentable by Saccharomyces cerevisiae (Baker's yeast). The synthesis sugar mixture, since it is a racemic mixture, must therefore contain 50 percent of one or more of the above sugars excluding sucrose. Consideration of the fact that the self-condensation of formaldehyde could give rise to eight racemic aldohexoses and at least four racemic ketohexoses not to mention pentoses and tetroses, it is rather surprising that the composition of the product is so relatively simple. It may well be that the same factors operate in the condensation of formaldehyde which lead, in natural products, to a preponderance of the aldohexose glucose and the ketohexose fructose. The important factor may be a steric one and there is considerable evidence to show that  $\alpha$ -D-glucose has the most stable conformational structure of the hexapyranosides (5). The structures of D-glucose, D-fructose, and D-mannose are closely related.



D-glucose



D-mannose



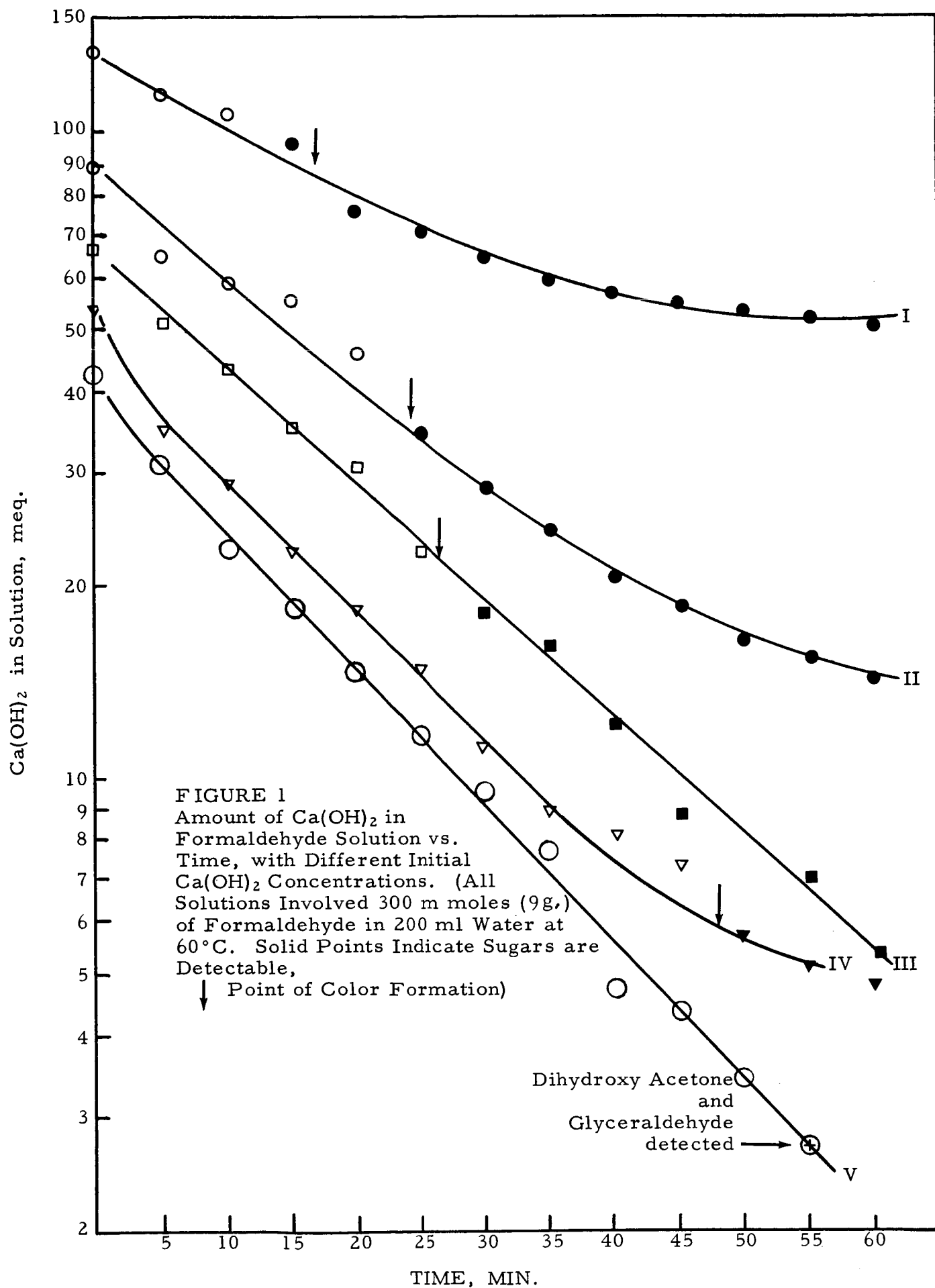
D-fructose

(acyclic forms)



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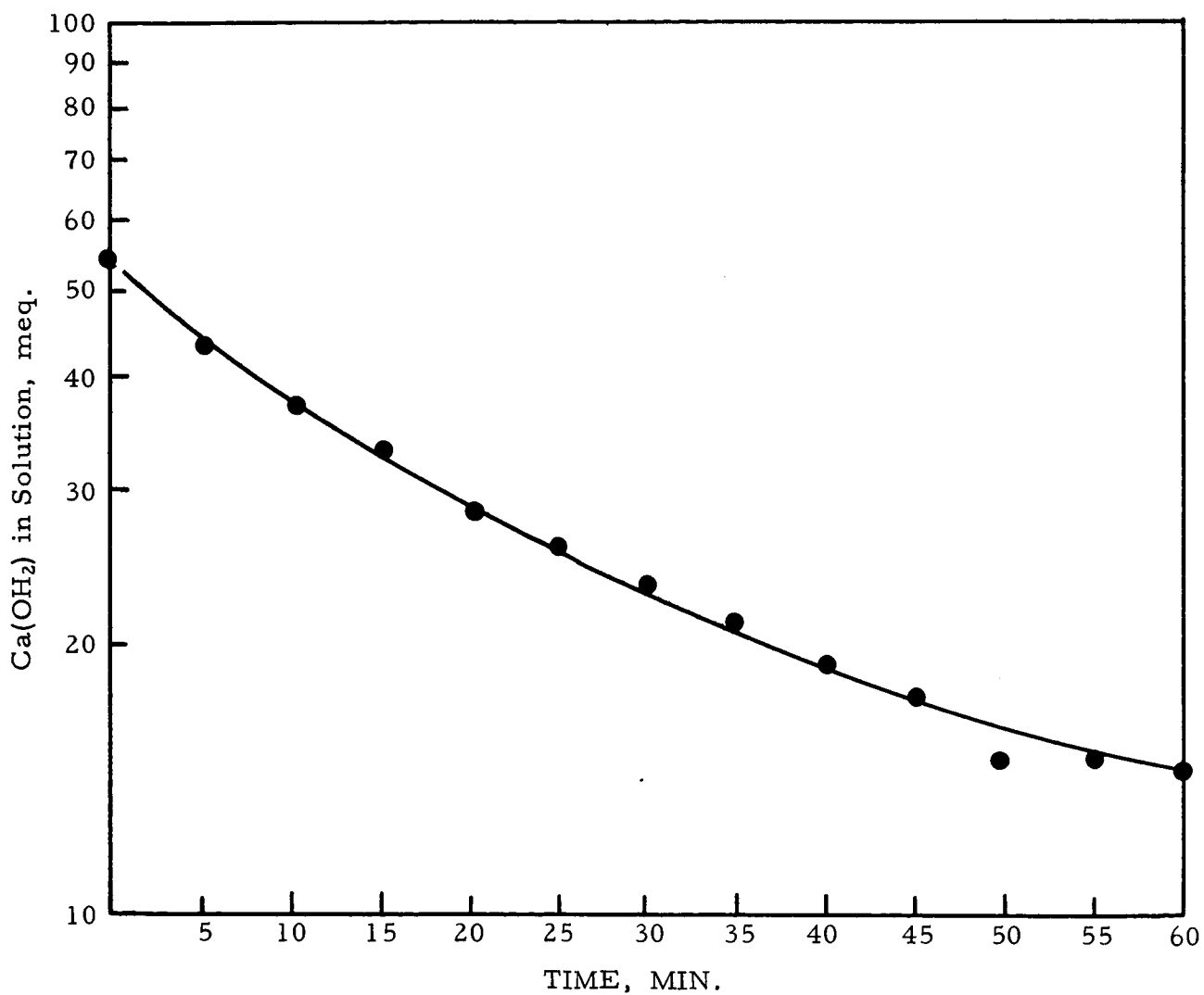


FIGURE 2. Amount of  $\text{Ca}(\text{OH})_2$  in D-Glucose Solution vs. Time at  $60^\circ\text{C}$ .  
Solution Contained 9 g. of D-Glucose in 200 ml Water.

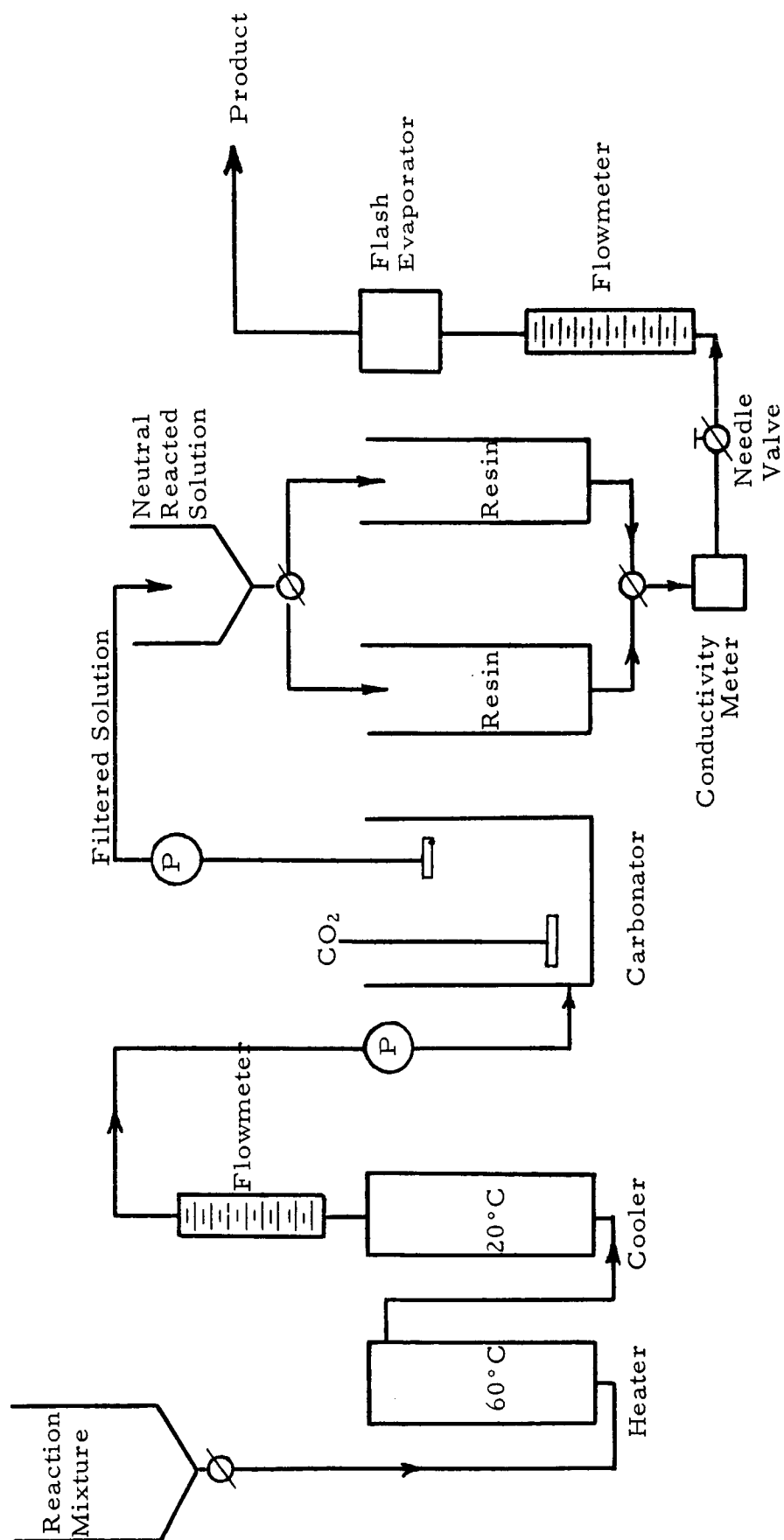


FIGURE 3: APPARATUS USED FOR THE CONTINUOUS PREPARATION OF SUGARS FROM FORMALDEHYDE SOLUTIONS

## CHAPTER 7. ANALYSIS OF FORMALDEHYDE SUGARS

### I. Analysis of the Sugar Mixture

A more detailed analysis of the synthetic sugar mixture prepared by the condensation of formaldehyde in the presence of lime has been made. When a chromatogram of the material was run on filter paper using butanol, acetic acid and water (4:1:5 w/v) as solvent, a continuous streak was obtained. This was detailed using aniline phthalate as spray reagent and colors were obtained ranging from yellow at the end nearest to the solvent front, through crimson in the middle of the streak, to brown near the starting point. This resembled closely the chromatogram obtained by Pfeil and Rückert (1, 2) and little information regarding the nature of the components could be obtained from it other than that trioses (yellow region), pentoses (crimson region) and hexoses (brown region) were present. A chromatogram was therefore run, the paper dried and then returned to the chromatography tank for another run and then this repeated once more. By this means, some separation of the mixture into discreet spots was achieved. The total number detected was thirteen. It is not known however if the slower moving spots represent individual compounds or mixtures. The faster moving spots are the compounds of lower molecular weight and since fewer isomers are possible, they are probably single substances. The type of chromatogram obtained is shown in Figure 1 and on it are also shown the positions in which authentic sugars were found. It will be seen that there is overlapping of the spots and the weak brown of fructose for instance is easily obscured by the strong crimson spot given by arabinose. An additional technique for further separation of the components is that of two dimensional chromatography and it is planned to apply this method to the sugar mixture. A clue to the identity of the materials in the spots is possible from the colors obtained with various spray reagents in particular with aniline phthalate, orcinol and trichloroacetic acid, resorcinol and hydrochloric acid and 2,5-diphenyl-3-p-styryl-phenyltetrazolium chloride (3). Thus with aniline phthalate, pentoses give crimson while hexoses give brown colors, and these are believed to be due to reaction of

the amine with furfural, hydroxymethyl furfural or their degradation products formed when sugars are heated with acid (4). The tetrazolium salt is reduced to a purple dye only by ketoses.

The colors obtained from the sugar mixture components and with some authentic sugars are shown in Table 1.

It is clear from the above results that the mixture contains aldo - and keto-hexoses, aldo- and keto-pentoses together with lower molecular weight compounds of which No. 3 is dihydroxy acetone. The following sugars have been suggested (5, 6, 7) as being present in the mixture:

Glycollic aldehyde

Glyceraldehyde, dihydroxyacetone

Tetroses

Xylose, Ribose, Ribulose, Arabinose, Lyxose, Xylulose

Fructose, Glucose, Galactose, Sorbose, Mannose

Dendroketose

The presence of DL-xylose and DL-arabinose in formose sugar has been proved conclusively by Hough and Jones (7) who isolated and characterized these sugars through the preparation of derivatives.

In order to determine the relative amounts of the materials 1 to 13 in the sugar mixture, 2 grams of it were separated on a column of cellulose using water saturated butanol as eluent. The eluate was collected on an automatic fraction collector and the identity of the fractions determined by chromatography of every fifth fraction on paper. Figure 2 shows the result obtained and the overlapping of the components of the mixture. To avoid such overlapping an impractically long column would be necessary. In Table 2, an estimate of the percentage composition in terms of components No's. 1 to 13 (Fig. 1) is given.

The major portion of the mixture is evidently contained in the pentose and hexose spots 7, 8, 9 and 10. The materials 3 to 12 all gave crystalline osazones, some of which had sharp melting points. The osazones were prepared from the column fractions, after further separation on a micro scale, on sheets of filter paper. An estimate of their molecular sizes was made by comparison with authentic osazones in circular paper chromatograms (8) and given in Table 2. The identity of the DL-osazones is difficult to

Table 1. Colors Obtained with Various Spray Reagents on the Synthetic Sugar Mixture Components and on Authentic Sugars

	Aniline Phthalate	Resorcinol- -HCl	Orcinol Trichlor- acetic Acid	Tetrazolium Salt	R <sub>a</sub> Value Dist. moved by compound Dist. moved by Dihydroxy acetone
13		Blue			
12	Brown	Brown			0.13
11	Brown	Brown-Black			0.23
10	Brown	Brown-Black			0.31
Glucose	Brown		Pale Yellow		0.36
9	Brown	Orange-Black	Yellow-Green	Purple	0.39
Sorbose	Brown	Pink	Deep Yellow	Purple	0.42
8	Crimson	Orange-Pink	Gray-Blue	Purple	0.43
Fructose	Pale Brown	Orange-Yellow	Deep Yellow	Purple	0.48
Mannose	Yellow Brown	Pale Yellow	Pale Yellow		0.51
Arabinose	Crimson	Pale Blue	Pale Blue		0.52
7	Crimson	Brown-Black		<u>Purple</u>	0.55
Xylose	Crimson	Pale Blue	Pale Blue		0.56
6	Crimson	Deep Blue	Blue		0.66
Ribose	Crimson	Pale Blue	Pale Blue		0.67
5	Yellow Orange	Green-Black	Green	<u>Purple</u>	0.74
Rhamnose	Brown Orange	Yellow-Brown	Pale Yellow		0.82
4	Yellow	Yellow		<u>Purple</u>	0.84
3	Yellow	Pale Green		<u>Purple</u>	1.00
Dihydroxy Acetone	Yellow	Pale Green	Pale Pink	<u>Purple</u>	1.00
2	Yellow	Yellow		<u>Purple</u>	1.14
1	Yellow	Yellow			1.31

Aniline Phthalate: - Brown with Hexoses, Crimson with Pentoses

Resorcinol-HCl: - Blue with Keto-pentoses, Red with Keto-hexoses

Orcinol-T.C.A.: - Blue with Keto-heptoses

Tetrazolium Salt: - Purple with Ketoses, no reaction with Aldoses

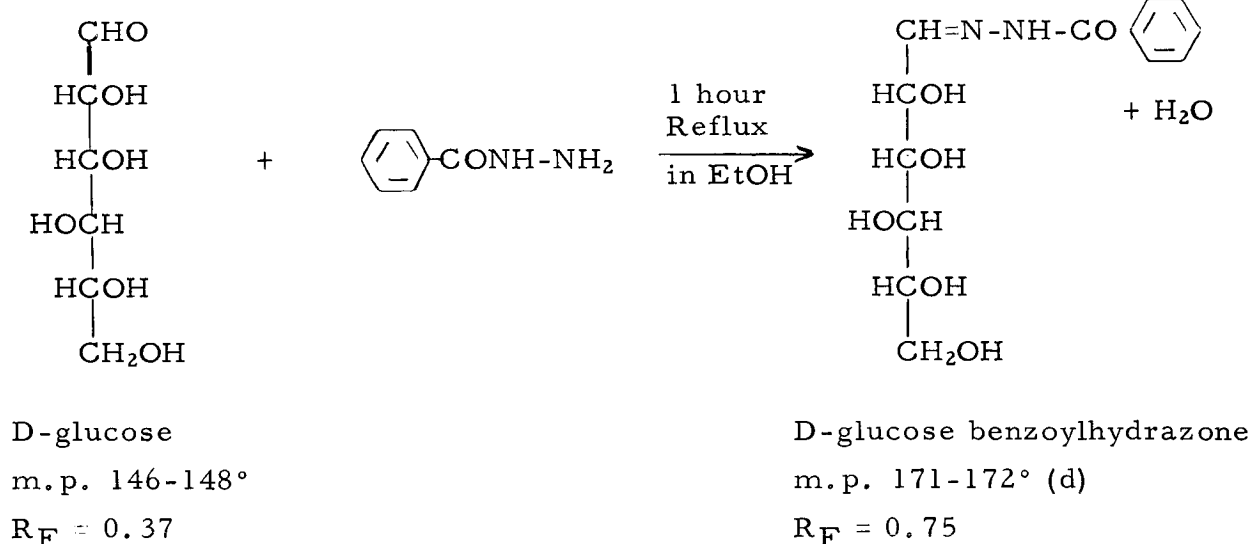
Table 2. Approximate Composition of the Sugar Mixture in Terms of the Components 1 to 13

<u>No. on Chromato-gram (Fig. 1)</u>	<u>Percentage by weight of mixture</u>	<u>Possible Identity</u>	<u>m.p. of Osazone</u>	<u>Molecular size of Osazone</u>
1	0.4	Glycollic Aldehyde		
2	1.1	Glyceraldehyde		
3	1.8	Dihydroxy-acetone	126-129°	Triosazone
4	3.2	Erythrose, Threose Erythulose	147-149°	Tetrosazone
5	2.5	Xylulose	183-187°	Pentosazone
6	6.5	Ribose, Dendroketose	159-176°	Pentosazone
7	17.2	Xylose	186-188°	Pentosazone
8	16.5	Fructose, Mannose	173-177°	Hexosazone
9	17.5	Sorbose, Arabinose	147-149°	Hexosazone
10	16.8	Glucose	183-185°	Hexosazone
11	8.5	Galactose	142-144°	Hexosazone
12	4.4		167-179°	Hexosazone
13	<2	A Heptulose		



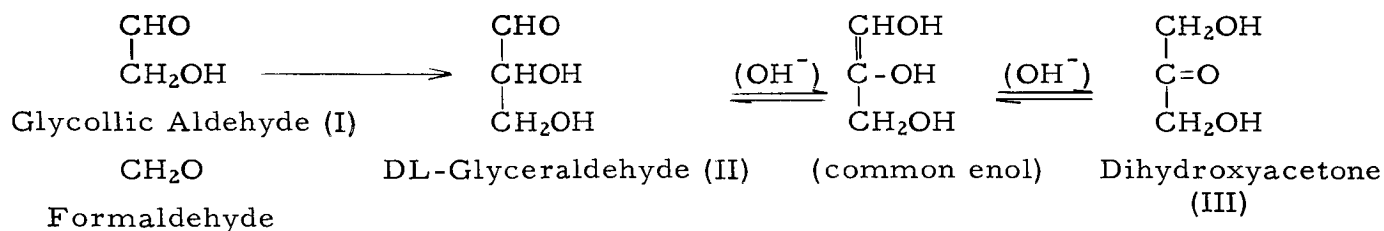
establish since both the crystal structure and m.p.'s of the racemates may be different from those of the optical isomers and not many DL-sugars are available for comparison purposes. DL-xylosazone, for instance, melts 40° higher than D-xylosazone (9) while the melting points of DL-arabinosazone and D(or L)-arabinosazone differ very little although they have different crystalline appearances.

The benzoylhydrazone of DL-arabinose is readily prepared and is easy to crystallize. Further, the free sugar may be regenerated by treatment of the hydrazone with benzaldehyde (7). D-Xylose and D-glucose also form derivatives readily and we are considering using this reagent (Benzoyl hydrazine) as a means of converting the sugar mixture into a mixture of hydrazones from which it may be possible to obtain the crystalline components by column chromatography. A preliminary experiment has shown that the benzoyl-hydrazones of D-glucose and D-arabinose for example, run as discreet spots on paper and are easily separated. The hydrazones give the same colors with aniline phthalate as do the parent sugars. A basic solvent system such as butanol, pyridine and water (45:25:40 v/v) is necessary for their chromatography since decomposition occurs in acid media. The hydrazones run much faster on the chromatogram than do the sugars.



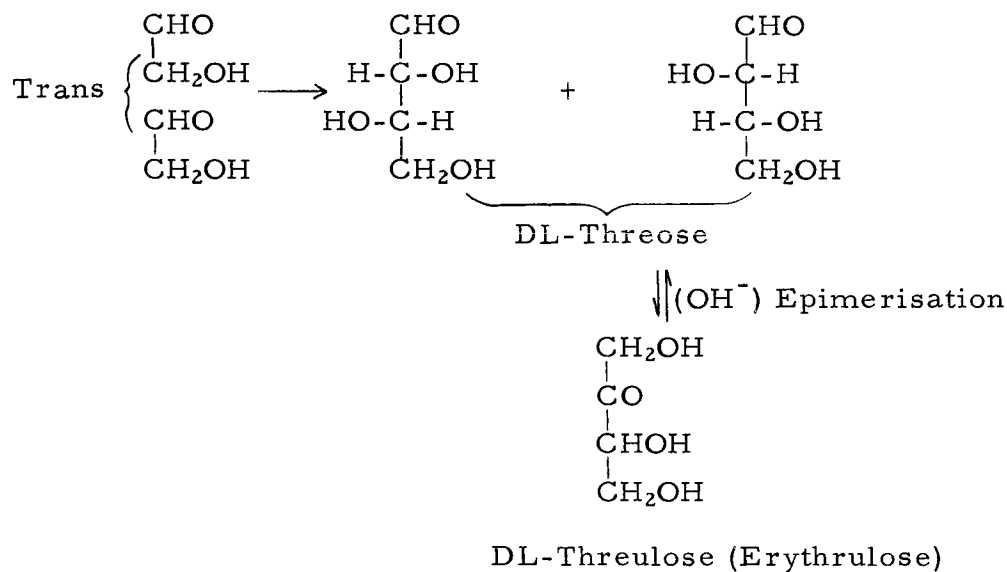
Further work on the analysis of the sugar mixture will be carried out as indicated above using this type of reagent which is readily prepared from the ethyl ester of a carboxylic acid, in this case ethyl benzoate, and hydrazine.

In the following, some predictions are made as to the type of compounds which are expected to be most likely present in the formose sugar. These predictions are based on the observation that the asymmetric synthesis favors the formation of trans hydroxyl groups for the two new asymmetric centers formed by aldol condensation (10, 11, 12, 13). The initial product of the formaldehyde condensation reaction is glycollic aldehyde and under certain conditions, it can be obtained in 50 percent yield (14). The mechanism of this reaction, upon which the whole "formose" synthesis is built, remains obscure (15, 16). The formation from glycollic aldehyde of glyceraldehyde is an orthodox aldol condensation and epimerisation under alkaline conditions of glyceraldehyde to dihydroxyacetone is well known.

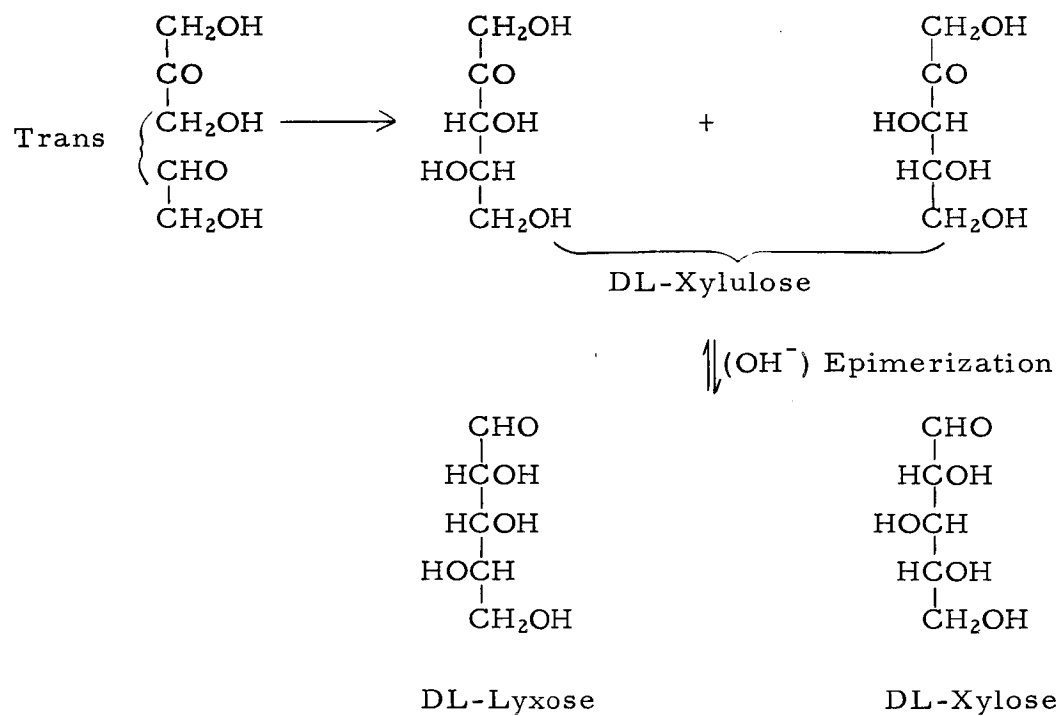


The three substances, I, II and III above are capable of being used as building blocks for a variety of sugars as follows:

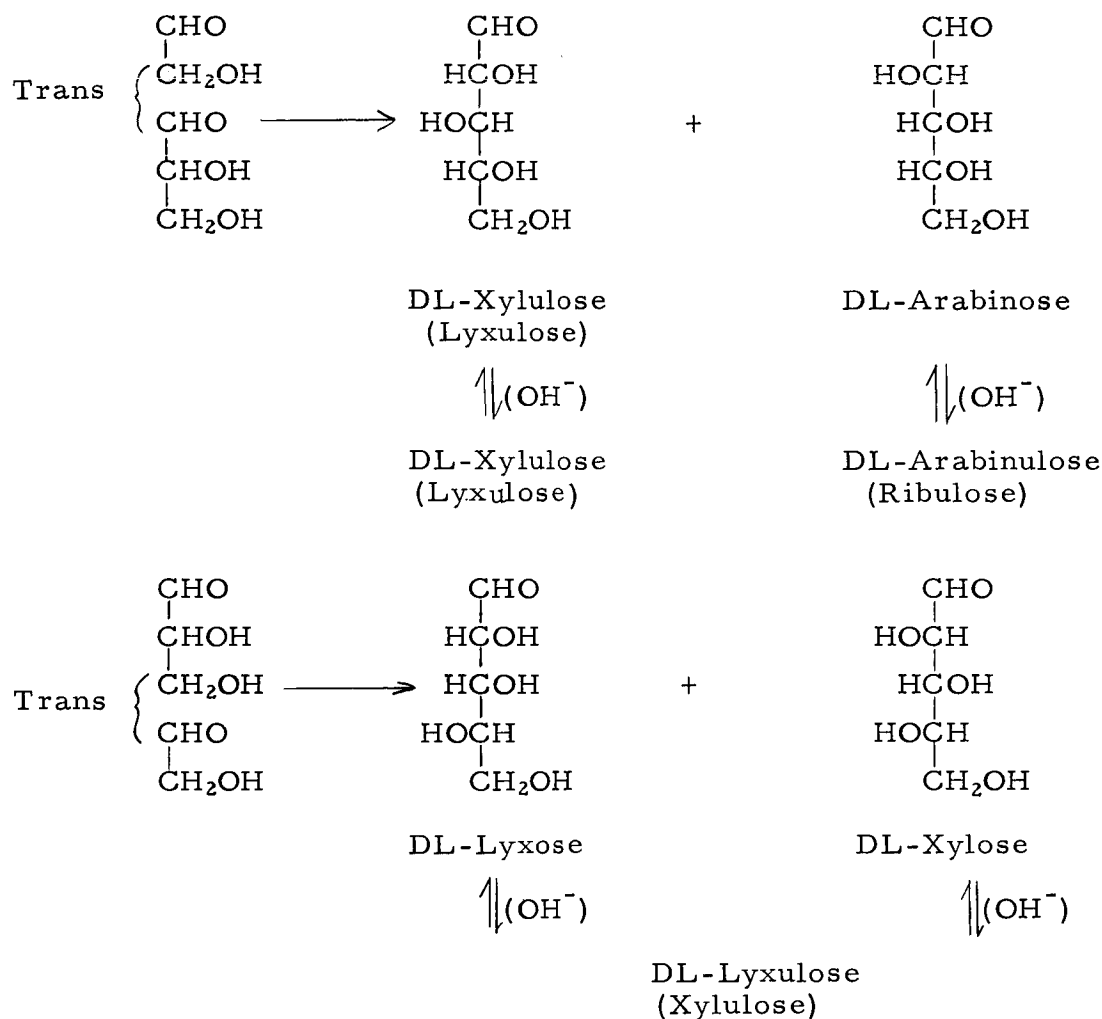
#### Self-Condensation of Glycollic Aldehyde (Formation of Tetroses)



Condensation of Dihydroxy-acetone with Glycollic Aldehyde (Formation of Pentoses)



Condensation of DL-Glyceraldehyde with Glycollic Aldehyde (Formation of Pentoses)



Hough and Jones (7) condensed, in the presence of barium hydroxide, both glyceraldehyde and dihydroxyacetone with glycollic aldehyde and detected in the products, all four pentoses (ribose, lyxose, xylose and arabinose). Xylose and arabinose predominated in the mixture. From the above scheme for the preparation of pentoses one would expect a mixture in which xylulose, xylose, lyxose and arabinose would be the main components.



### Self Condensation of Glyceraldehyde

By the same considerations used in the above, this would be expected to lead to a mixture of DL-glucose, DL-idose, DL-mannose and DL-gulose.

In summary the expected formation from formaldehyde of the following sugars have been illustrated:

Threose, Threulose (Erythrulose

Xylulose, (Lyxulose), Lyxose, Xylose

Arabinose, Xylulose, Arabinulose (Ribulose)

Sorbose, Idose, Gulose

Fructose, Glucose, Mannose

Dendroketose

## II. Preparation of Formose Sugar

Work has continued on the preparation of sugars from formaldehyde. It was found earlier that cellulose powder is an effective catalyst in the alkaline condensation of formaldehyde and it was hoped that the cellulose might affect the steric course of the reaction and possibly produce some optical activity in the product. This however was not the case. The product obtained in the presence of a large amount of cellulose powder had no optical activity and gave a paper chromatogram identical to that obtained in its absence. It has also been found possible to obtain the same sugar mixture with increased concentrations of formaldehyde up to 38 percent. At this concentration, the reaction, following the usual induction period, was violently exothermic.

The apparatus for the continuous preparation of sugars, has been improved by the use of an all glass spiral for the reaction vessel and by the use of a centrifuge for the separation of recovered calcium carbonate. Four pounds of sugar mixture were made in the new apparatus and submitted for feeding tests. The reaction conditions employed were the same as those described for the continuous operation described in the previous quarterly report.

### III. Feeding Experiments with the Synthetic Sugar

The results of the feeding tests on rats are given in Appendix 1. These tests were carried out in the Biochemical Testing Center of Bio-Dynamics, Inc., Edison, New Jersey, under the direction of Dr. T.J. Russell. The results were disappointing especially in view of the fermentability of the mixture by baker's yeast. The toxicity of the sugar for weanling rats has precluded any estimation of its nutritional value in these animals. Mature rats, however, are less adversely affected by the diet and it is hoped to obtain some information on the nutritional value of the mixture from a feeding list on adult rats currently in progress.

An investigation of the source of the toxicity is being made and though formaldehyde has been detected in the syrup, the amount present (about 0.1 mg./g.) is insufficient to account for the effects observed in the animals (see Appendix report). The sugar mixture has been fractionated on a column of cellulose on a larger scale than that described in the analytical section above and it is intended to feed each fraction to individual weanling rats by stomach tube. This should make possible an identification of the type of material responsible for the toxicity.

This may turn out to be a sugar such as D-xylose which has been shown to be present in "formose" sugar (7) and which has also been shown to have toxicity for weanling rats (18). The symptoms obtained with this pentose, diarrhea and abdominal distension, are similar to those described by Dr. Russell. In contrast to D-Xylose, its keto epimer, X-xylulose which is also very probably present in the synthetic sugar, is definitely utilized by the rat (19).

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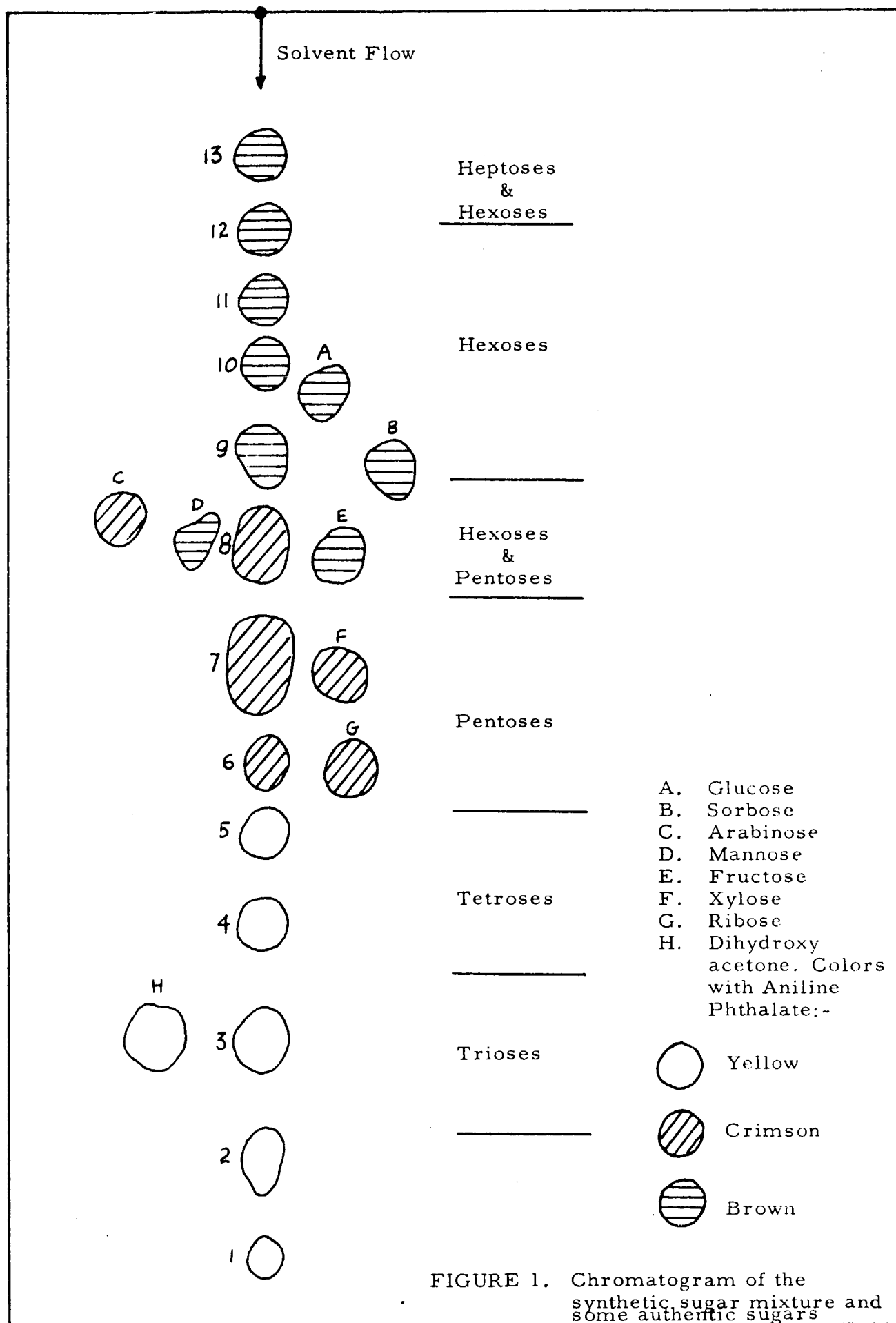


FIGURE 1. Chromatogram of the synthetic sugar mixture and some authentic sugars

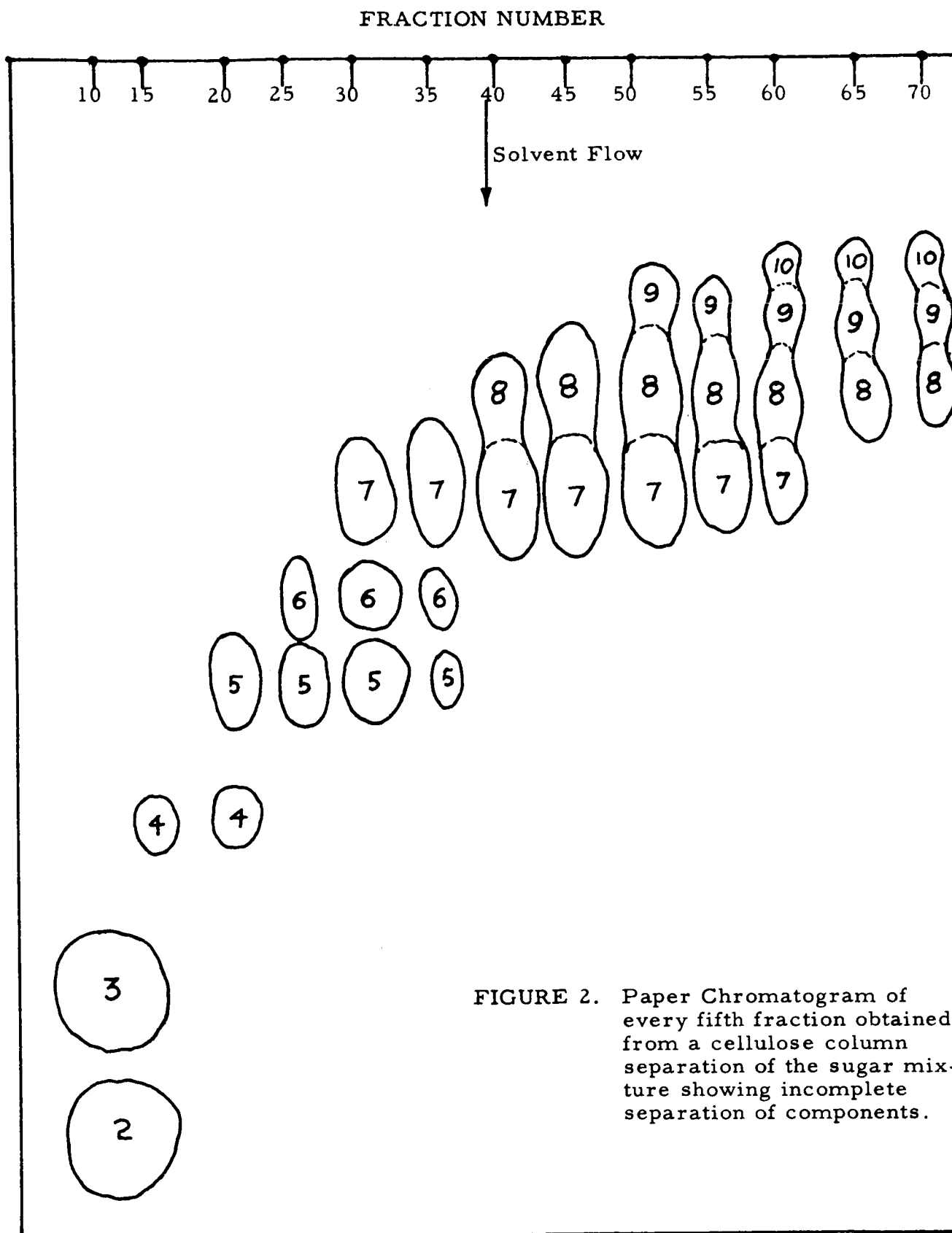


FIGURE 2. Paper Chromatogram of every fifth fraction obtained from a cellulose column separation of the sugar mixture showing incomplete separation of components.

## CHAPTER 8. FURTHER STUDIES OF THE TOXICITY, ANALYSIS AND PREPARATION OF FORMALDEHYDE SUGARS

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### I. Toxicity of the Sugar Mixture

In an effort to remove or identify the toxic material in the synthetic sugar mixture prepared by the self-condensation of formaldehyde in the presence of calcium hydroxide, various separation techniques were applied.

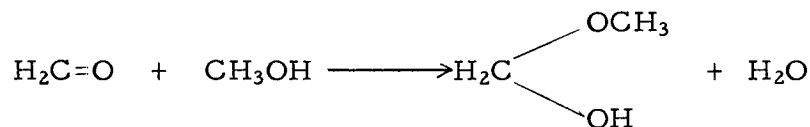
(a) A 25 percent solution of the syrup in 95 percent ethanol was treated with an equal volume of ether and thereby separated into approximately equal weights of insoluble and soluble materials. Paper chromatography of the two fractions showed that no clear cut separation had occurred but that the colorless precipitated material contained a diminished amount of lower molecular weight products (No's. 1 to 6 in Figure 1, Chapter 7), while the yellow soluble material showed a preponderance of these substances.

Feeding tests were carried out with these materials both by intubation and by incorporation in a diet. No significant difference in the time of onset of the toxic symptoms were observed between either material although there was an indication in one experiment that the insoluble material was less toxic.

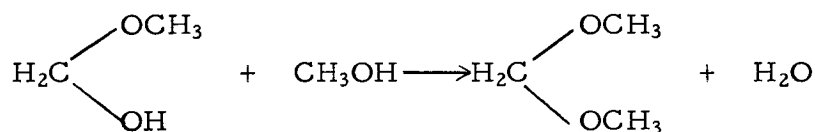
(b) A 10 percent aqueous solution of the sugar mixture was extracted continuously with ether for two weeks. This removed about 20 percent of the mixture and analysis of the material remaining in the aqueous phase showed that it was depleted in the lower molecular weight components. Again, however, the fractions showed no difference when fed to rats.

(c) Twenty grams of the sugar mixture were fractionated by passage in butanol through a column of cellulose powder. The fractions obtained were then grouped into three mixtures containing the materials in the lower, middle, and upper parts of the chromatogram shown in Figure 1, Chapter 7. There was insufficient material in the individual components from 20 grams of mixture for a feeding test to be made.

No differences were found in either of these three fractions when fed to rats. It appears, therefore, that there are toxic materials associated with each component of the mixture. This is hard to explain unless the adverse symptoms are due to sugars of the "unnatural" configuration. A further possibility is that the components of the mixture are all compounds of the various sugars and formaldehyde and that the toxicity is due to a release of the formaldehyde in the animal body. Alcohols react with formaldehyde to form in neutral or alkaline solution, hemiacetals as follows:



and under acidic conditions, to give formals:



Apparently sugars, which are polyhydroxy compounds, react in much the same manner to give unstable hemiacetals in neutral or alkaline solution (1, 2, 3, 4, 5, 6) and the more stable methylene ethers or formals in the presence of strongly acidic catalysts (7, 8). Thus bioses such as maltose, sucrose and lactose yield colorless crystalline compounds containing varying amounts of formaldehyde when the bioses are dissolved in the minimum amount of aqueous formaldehyde at 70°C (9). The products are stated to be without sharp odor but dissolve readily in water yielding formaldehyde and sugar.

The synthetic sugars were made under alkaline conditions, consequently any sugar-formaldehyde compounds would only be of the unstable hemiacetal type and when dissolved in water would be decomposed. Analysis of aqueous solutions of the synthetic sugar mixture has shown only very low levels of the order of 0.1 mg. per gram of sugar mixture. This amount of formaldehyde could not produce the reaction observed in the experimental animals. Further, treatment

of the sugar mixture with 10 percent sulphuric acid at 60°C to hydrolyze any formals which might have been present, gave a formaldehyde content of only 0.2 mg. per gram. When weanling rats were fed a complete synthetic diet containing 4 mg. of formaldehyde per gram of diet sugar, slight weight losses were observed but no other systemic effects were grossly observable.

## II. Alternative Method of Preparation of Formose Sugar

With a view to producing a more acceptable sugar mixture, a patented process using a solution of lead oxide in sodium hydroxide as condensing agent, was examined. This method required less inorganic material per gram of formaldehyde and could be used with 30 percent solutions of formaldehyde. It required higher temperatures and longer time of reaction than the lime process. Comparable data for the two processes are shown in Table 1.

Table 1. Comparison of the Lead and Lime Processes

<u>Reactants</u>	<u>Water (liters)</u>	<u>Temp.</u>	<u>Time of Reaction</u>
100 g. formaldehyde 24.7 g. Ca(OH) <sub>2</sub>	2.22	60°C	10 min.
100 g. formaldehyde 0.4 g. P60 5.1 g. NaOH	0.67	90°C	8 hrs.

The formose sugar solution made using lead was deionized using a mixed bed resin as before and concentration of the solution gave a clear colorless sweet tasting syrup. No lead was detectable in the syrup which was fermentable in part by baker's yeast. Paper chromatography of the product showed that it was essentially the same as the product from the lime reaction. The product made with lead contained more dihydroxyacetone and less of the hexoses. No improvement was observed in feeding experiments with this new mixture.

### III. Analysis of Synthetic Sugar Mixtures

#### A. Sugars

The reaction of benzoylhydrazine with sugars to form benzoylhydrazones has been found to occur with a number of aldoses, but not with the two ketoses sorbose and fructose. The colors given by the hydrazones with aniline phthalate were the same as the parent sugars. Their  $R_A$  values are given in Table 2.

Table 2.  $R_A$  Values of Sugars and Their Bz Hydrazones

<u>Compound</u>	<u><math>R_A</math> (Sugar)</u>	<u><math>R_A</math> (Derivative)</u>
Dihydroxyacetone	1.00	1.40
Glyceraldehyde	1.00	1.34
Xylose	0.78	1.22
Mannose	0.705	1.15
Arabinose	0.69	1.19
Fructose	0.675	none
Glucose	0.635	1.16
Sorbose	0.63	none

Solvent: Butanol (45), Pyridine (25), Water (40)

The hydrazones studied all had an  $R_A$  value greater than 1, i. e. they moved faster than dihydroxyacetone on paper chromatograms and could be easily separated from nonreacting sugars.

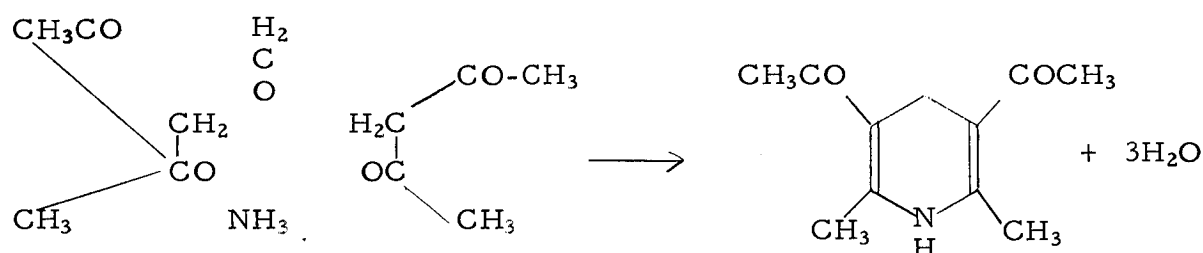
When the two synthetic mixtures prepared using lime and lead respectively were treated with benzoylhydrazine, hydrazones were formed and on paper chromatography they moved as one large spot owing to the closeness of the  $R_A$  values. With the lime produced sugar, two weak spots remained corresponding to unreacted sugars and their positions on the chromatogram indicated that the spots were due to fructose and sorbose. The sugar made with lead reacted completely with benzoylhydrazine and hence appears not to contain the two ketoses.

This method of analysis should prove to be very useful for the identification and separation of the components of the complex formose sugar mixtures.

### B. Formaldehyde

The estimation of formaldehyde using chromotropic acid (11) cannot be applied directly to sugars since in the strong sulphuric acid required for the determination, they are dehydrated to carbon. This is an efficient adsorbent for the violet compound produced in the reaction of formaldehyde with chromotropic acid. When a solution of the sugar mixture in 0.5 N hydrochloric acid was distilled, formaldehyde was detected in the distillate but recoveries when known amounts of formaldehyde were added, were poor. The method was therefore unreliable but did give a rough estimation of about 1 mg. of formaldehyde in 1 g. of sugar mixture.

A method which obviates the use of strong acid is that of Nash (12) in which formaldehyde is detected by the yellow dihydrolutidine derivative which it forms with ammonia and acetylacetone:



The reaction is carried out in neutral solution at 60°C and the product estimated by its U.V. absorption at 412 mu. Analyzed by this method, C-783-88 (see key in the appendix) gave the low formaldehyde content of 0.08 mg. per gram and this was raised to only 0.2 mg. per gram after first heating the mixture with 10 percent sulphuric acid to hydrolyze any formals present.

#### IV. Inhibition of Baker's Yeast by Formaldehyde

The synthetic sugar mixtures were fermentable by yeast and could therefore not contain much formaldehyde since this inhibits yeast fermentation as the following experiment showed.

A 10 percent solution of D-glucose in a suspension of yeast in 1 percent aqueous disodium hydrogen phosphate was treated with varying amounts of formaldehyde. Fermentation was estimated by the amount of carbon dioxide generated after a given time. None occurred when formaldehyde was present at a level of 76 mg. per gram of glucose. Levels of 0.04 mg., 0.1 mg., 0.2 mg., and 0.4 mg. were insufficient to prevent fermentation but showed decreasing amounts of carbon dioxide.

#### V. Summary

It has not yet been possible to identify the toxic components of formose sugar. The indications are that there are a number of toxic components present and that the overall toxic effect may be due to a cumulative action of sugars of both uncommon structure such as dendroketose, and of unnatural configuration such as L-fructose, D-sorbose, etc. Speculation on these lines is difficult owing to the paucity of biological data on such compounds but it is known for instance that even some of the "natural" sugars such as D-xylose and D-galactose can produce adverse effects in experimental animals. There also remains the possibility that if the feeding tests were carried out in other animals (in place of rats), improved results might be obtained.

It is clear that future efforts on the synthesis of sugars from formaldehyde will have to be concentrated on methods leading to less complex mixtures. Some ideas on these lines have been proposed (Proposal 11-2-62 for continuation of NASr-88). Hitherto, the processes used have been chosen because of their simplicity from a preparation point of view. It is believed now, however, that the synthetic problem of producing non-toxic sugars is a very difficult one and that it should be solved first without consideration of the process adaptability to the requirements of a space vehicle. Only when the factors of toxicity are understood can the question of feasibility be satisfactorily answered.



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APPENDIX I

ELEMENTARY ASPECTS OF THE GENERATION  
OF VARIOUS TYPES OF ELECTRIC DISCHARGES

by G.C. Akerlof

CONTENTS

1. The passage of an electric current through a gas.
2. The migration of ions and electrons in a gas under the influence of an electric field.
3. The Townsend discharge at low pressures.
4. The self-sustained glow discharge.
5. Thermal equilibrium in a glow discharge plasma.
6. The self-sustained arc discharge.
7. Electrodeless discharges.
  - A. Physical characteristics.
  - B. Characteristics of some chemical phenomena.

1. The Passage of an Electric Current Through a Gas

The passage of electricity through an ordinary conductor like let us say a metal wire is governed by Ohm's law stating that the ratio between potential drop and current is constant. A metal may be imagined to consist of a lattice structure of positive ions between which the electrons move with ease. When a potential difference is impressed between the ends of a wire the positive ions remain in place but the electrons move from the negative towards the positive end under loss of energy acquired from the electrical field and appearing as heat.

This simple picture of the passage of electricity through metals contrasts sharply to the complicated phenomena taking place when a current passes through a gas. The molecules of a gas are electrically neutral and although the individual atoms forming a molecule consists of a positive nucleus surrounded by a number of electrons these are all held in definite orbits by strong forces and even at considerable field strengths a gas is an excellent insulator. However, when at an adequate field strength electrons and ions begin to form, as will be discussed later, a series of very complicated events occur. In a gas it is not only the electrons that move under the influence of the electric field. The positive ions distributed more or less at random will also start to move but in opposite direction to that of the electrons. On account on their greater mass, the rate of migration of the positive ions is a small fraction of that of the electrons. If equal numbers of electrons and positive ions are liberated, the latter will remain a much longer time in the discharge space and create a positive space charge distorting the field between anode and cathode. The field strength along the path of the discharge is not constant as in the case of conduction through a wire, but varies from point to point.

In a gaseous discharge the electrons collide with freely moving molecules giving rise to such processes as elastic or sticky collisions, excitation, ionization, and even the formation of negative ions. The excited molecules and ions produce in turn secondary effects like radiation of light. Positive ions may release electrons from the cathode and when colliding with molecules causing large changes in their kinetic energy,

excitation, ionization or recombination with electrons to form neutral species. In all discharges heat is generated as shown by increasing temperature of the gas and the electrodes. Figure 1 may serve as an illustration of the highly complex nature of conduction of electricity through a gas as compared to conduction in a metal. One complexity is caused primarily by the fact that gas molecules have a random motion. When an electron collides with a gas molecule there are only two particles involved, while in a metal its entire lattice participates. The complex nature of a gaseous discharge is not due to the elementary processes as such, but to the great number of different processes possible.

## 2. The Migration of Ions and Electrons in a Gas Under the Influence of an Electric Field

The charge of an electron  $e$  is equal to that of a singly charged ion or  $1.60 \times 10^{-19}$  coulombs and a given electrical field exerts a force of equal magnitude on either. However, the mass  $M$  of a positive ion with the molecular weight  $A$  is  $1840 \times A$  times larger than the mass  $m$  of an electron. Therefore, in a given electrical field the acceleration, or force divided by mass, is very much larger for the electron than for the ion. Between two points with the potentials  $E_1$  and  $E_2$  the change of the kinetic energies of the electron and the ion in vacuum may be expressed by the equations:

$$1/2 m (v_2^2 - v_1^2) = e (E_2 - E_1)$$

$$1/2 M (v_2^2 - v_1^2) = e (E_1 - E_2)$$

where  $v_1$  and  $v_2$  denote initial and final velocities respectively. In the case of a chlorine ion with an atomic weight of 35.5 and  $M/m$  ratio of 65380 and zero initial velocity, when passing through a potential difference of one electron volt or  $1.60 \times 10^{-12}$  ergs will acquire a velocity of 1.67 Km/sec., while an electron under the same circumstances will have a speed of 600 Km/sec. In a gaseous discharge the electrons thus

carry the entire current except for the small fraction contributed by the positive ions.

To describe what happens when charged particles collide with neutral particles in a gaseous discharge we must differentiate between elastic and inelastic collisions. In the case of the former, the species colliding with an electron retains its structure but acquires larger kinetic energy or, in other words, their temperature is raised. Inelastic collisions on the other hand change the internal structure of the species present which will show itself in a series of different phenomena. The fraction of its kinetic energy an electron may transfer in an elastic collision is quite small. For a central collision it amounts to  $4 m/M$  but the statistical average is equal to half this value. In the case of an electron colliding with a chlorine molecule these values would thus be  $3 \times 10^{-5}$  and  $1.5 \times 10^{-5}$  respectively. When an ion collides with a neutral species of the same mass it would be able to transfer its entire kinetic energy in a central collision or about half the amount as a statistical average. The difference between the central collisions of electrons and ions with neutral particles is illustrated in Figure 2. On account of their large mass and incessant collisions the ions are generally unable to attain sufficient kinetic energy to excite or ionize neutral species present while the electrons, in spite of numerous collisions, retain most of theirs and, above certain levels, they do cause such phenomena to occur.

According to the precepts of the quantum theory, an atom may exist in a definite number of higher energy states or energy levels. As long as an electron has a kinetic energy smaller than the lowest state of excitation any collision taking place would be elastic but as soon as this limit is exceeded there is a definite chance that excitation will occur and when this happens the electron will lose an amount of energy equal to the excitation energy, which also applies to the generation of higher excited states. An excited atom returns as a rule to a lower or the ground state after a time of the order of  $10^{-8}$  seconds. The energy released is equal to  $e(E_2 - E_1)$  and it is emitted in the form of a radiation quantum with a wavelength given by the equation:

$$E \lambda = 3 \times 10^{18} h = 12400$$

where  $E$  is expressed in electron volts,  $\lambda$  in Angstrom units and  $h$  is the Planck constant  $6.62 \times 10^{-27}$  erg seconds. Some excited states are metastable and have a life time that may extend to 0.1 second or even longer. According to the quantum theory, these states are unable to return to the ground state by radiation of energy but they may do so on the walls of the enclosing chamber or by ionizing atoms of other species present with a lower ionization energy. The formation of metastable states may in this manner make a large contribution to the ionization of a gas.

### 3. The Townsend Discharge at Low Pressures

A self-sustaining discharge with currents of a few microamperes may be obtained between parallel electrodes at low gas pressures and with resistances of several megohms. Even a strong electrical field is unable to remove electrons from a particle present in a gas, but electrons are liberated continuously in minute quantities by the ever present cosmic rays. An electron liberated near the cathode is accelerated by the electric field and generates on its path other electrons due to ionization of neutral species. The first pair of electrons thus formed are in turn able to ionize still more atoms and a steady repetition of this process causes an avalanche of electrons to migrate toward the anode. However, energy losses occur due to elastic collisions and simple excitation reducing the number of electrons present in the avalanche. If primary electrons are formed at a rate of one per second this would give a current of about  $10^{-16}$  amperes but in reality the values observed are  $10^{10}$  times larger or about  $10^{-6}$  amperes. Besides the primary electrons there are also formed secondary electrons in the Townsend discharge. In the avalanche there are generated just as many positive ions as electrons. When the ions hit the cathode they neutralize the same number of electrons but they are also likely to generate an excess number. If this number of additional electrons liberated by all the ions formed in the first avalanche from a single electron is equal to  $g$ , the second

and successive avalanches are each multiplied with  $g$  until the magnitude of the current is limited by the resistance of the discharge circuit.

#### 4. The Self-Sustained Glow Discharge

We have described how the electric breakdown of a gas at low pressures initiates a Townsend discharge with currents of a few microamperes. As illustrated diagrammatically in Figure 4, there exists in the range between this type and high current arc discharges an intermediate type which has been called glow discharges using currents measured in milliamperes. In Figure 3 the voltage  $V$  has been plotted on a linear, the current  $I$  on a logarithmic scale. The breakdown voltage of the Townsend discharge is designated by  $V_C$ , the normal cathode potential drop by  $V_n$  and the arc voltage by  $V_d$ .

The appearance of the glow discharge is quite different from that of either the Townsend or the arc discharges. It is divided up in a number of parts with widely different properties as shown by their luminous behavior. The relative luminous intensities of the main sections of a glow discharge are indicated in Figure 4a by the density of the hatching. Figure 4b gives a diagram of the variation of the potential between anode A and cathode C in a gas atmosphere. The length of the positive column increases with the length of the discharge while the phenomena occurring at the cathode remain virtually unchanged.

In many respects the mechanism of the glow discharge is the same as that of the Townsend discharge. The electrons leaving the cathode form positive ions (and light quanta) which migrate to the cathode and release more electrons. A self-sustained discharge must have a multiplication factor equal to or greater than unity. In the Townsend discharge the breakdown voltage is related directly to the entire distance between anode and cathode. In the case of a glow discharge it is given mainly by the distance CM in Figure 4a and the total voltage drop is approximately equal to the minimum value of the breakdown voltage. The electrons traveling beyond the distance CM enter a practically field free space and some of them have acquired quite high velocities. They lose energy in collisions with molecules causing

excitation, which is the cause of the negative glow, dissociation and ionization. Coming out of the negative glow and entering the Faraday dark space the electrons do not have sufficient energy to cause luminous excitation.

The positive column adjoins the Faraday dark space. It forms when the anode and cathode are sufficiently far apart and may either be homogeneous throughout its entire length or be striated exhibiting alternate dark and light layers which either may be stationary or moving forward at high velocities. The column may however also under certain conditions wriggle around in a most erratic manner. By measuring the changes as the length of the column is varied, the potential difference per unit length of the column may be determined and thus also the strength and gradient of the electric field. In a homogeneous positive column the field strength is constant indicating that it contains equal numbers of electrons and positive ions in any given volume. If  $n$  electrons are present per cc and they are moving towards the anode at an average velocity of  $V_e$  cm./sec. they represent a current density of  $n.V_e.e$ . The positive ions present in an equal number have the velocity  $V_p$  and the total current  $j$  is given by the equation:

$$j = n.e (V_e + V_p)$$

The velocity of the electrons is very much larger than that of the positive ions and therefore the current is almost entirely carried by the electrons.

The determining factor with regard to the number of electrons present in the positive column is their rate of recombination with the ions on the wall of the discharge tube particularly at lower pressures. In a self-sustaining discharge the losses of electrons in the positive column must be made up by ionization due to collisions in the gas. It is thus necessary that each electron during its travel through the positive column must cause one ionization to maintain a steady current. Probe measurements have shown that the velocities of the electrons show a Maxwellian distribution. The average energy  $\bar{W}$  of gas molecules at an absolute



temperature  $T$  is given by the equation:

$$\bar{W} = 3/2 kT$$

where  $k$  is the Boltzmann constant. The application of this equation allows the assignment of a certain temperature  $T_e$  to the electrons present in the positive column. Generally,  $T_e$  has been found to have an order of magnitude of  $10,000^\circ\text{K}$  or higher. The temperature of the gas in which the column is formed remains at approximately its initial level until the potential applied is raised above the minimum sustaining level. The non-equilibrium between the temperatures of the electrons and the gas is due to the acceleration of the electrons in the electric field causing them to yield only small amounts of energy in elastic collisions with gas molecules. However, when the electrons acquire sufficient energy to cause excitation they will suffer considerable energy losses.

##### 5. Thermal Equilibrium in a Glow Discharge Plasma

A gas stream in which a sustained glow discharge takes place contains a variety of species, electrons, ions, atoms, and neutral molecules. Such a gas, where charge carriers are present at high concentrations, has been called a plasma. It obeys the ideal gas laws, and, at higher pressures, local thermal equilibrium is established. Full equilibrium exists when the frequency distribution of the energy states follows Boltzmann's law. This occurs only in a gas where wall effects are eliminated and unbalanced energy additions or losses preventing attainment of equilibrium are absent.

The electrons (like also the ions) take up from the electrical field of strength  $F$ , per unit volume of gas, and unit of time, the energy  $e.N.v.F$ . where  $e$  is the charge of the electrons,  $N$  their number and  $v$  their velocity in the direction of the field. Collisions with heavier particles causes random distribution of their velocities and gives a uniform electron temperature which is established after only a few such processes. The length of time  $t$  of a collision of an electron with a heavier particle may be expressed by the equation (Rompe and Weizel, Theorie elektrischer Bögen and Funken, 1949):

$$t = \frac{1}{v_e(n_o Q_{eo} + n_i Q_{ei})}$$

where  $v_e$  is the thermal velocity of the electrons,  $Q_{eo}$  and  $Q_{ei}$  the cross section areas of the neutral molecules and the ions present with respect to the electrons. Rompe and Weizel have shown that, depending on the circumstances, a uniform electron temperature is attained in  $10^{-12}$  to  $10^{-17}$  seconds.

The length of time required for equalization of electron and gas temperatures is a function of the ratio of the mass of the electron  $m_e$  and that of the heavier particle  $M_n$  to which the surplus energy of the former is given off during each single collision. Since the ratio  $m_e/M_n$  has an order of magnitude of  $10^{-4}$ , a time interval of roughly  $10^{-5}$  to  $10^{-7}$  seconds would be sufficient. However, during their travel the electrons continuously pick up energy from the electric field giving rise to a finite difference between their temperature and that of the gas molecules. At the same time excitation and ionization processes increase the rate at which equilibrium is approached although recombination reactions tend to offset their effect and accelerate the rate at which a uniform electron temperature is reached.

Large temperature variations do occur, particularly at the border of all discharges, preventing the attainment of equilibrium. The disturbance would be small as long as the temperature difference across a distance of the mean free path  $\lambda$  is small compared to the values of the absolute temperature:

$$\frac{\text{grad. } \lambda T_x}{T_x} \ll 1$$

In the case of excitation and ionization phenomena, the corresponding values of  $\lambda$  may increase considerably and still not cause larger disturbances but even highly unstable species participating in chemical reactions that occur simultaneously often appear to be able to travel relatively long distances without recombination. Using adequate quenching of the gas stream, the synthesis of thermally unstable compounds like ozone, hydrazine, nitric oxide, acetylene, hydrocyanic acid and a number of others may

readily be carried out and give good yields in glow discharges with high electron temperatures. In the case of the presence of a solid phase with a large surface area like finely powdered carbon passing through the discharge, ion recombination reactions would proceed at a very high rate. Even at high velocities of formation of ions in a chlorine atmosphere the carbon surface would limit the average life expectancy of these ions to such an extent that even at fast quenching the few able to form carbon compounds would give low power yields.

#### 6. The Self-Sustained Arc Discharge

A non self-sustaining arc discharge with currents of several amperes may be initiated by the use of an incandescent cathode heated independently by a filament current. The self-sustaining arc was discovered by Davy about 1810 when he connected two horizontal carbon rods to the terminals of a battery, pressed their tips together and then drew them apart a short distance to obtain a discharge curved like an arc and giving off a very intense light.

In an arc between two carbon points both get very hot and the cathode loses electrons by thermionic emission. At small electrode separations only a low voltage is required to maintain the discharge. However, the behavior of this type of discharge is extremely complicated. To eliminate extraneous effects it has been studied mainly in a noble gas between tungsten electrodes. Where the temperature of the cathode approaches  $2500^{\circ}\text{K}$  a perceptible emission of thermionic electrons takes place from a tungsten surface lowering the number of positive ions required to maintain the discharge and the voltage across the arc drops.

When the temperature of the tungsten increases still further the number of thermionic electrons released also increases and they may soon supply the largest share of the electrons. Since the positive ions formed have a very much lower mobility than the electrons, they tend to set up a positive space charge in front of the cathode allowing the electrons to be released even more easily.

An arc discharge generates around itself a strong magnetic field. In the case of a cylindrical arc the magnetic force is oriented radially to its

axis and exerts a pressure on the charge carriers which has been called the "pinch effect". At higher pressures this effect is unimportant but as the pressure decreases its relative value increases. Its use is being studied to bring about the fusion of hydrogen nuclei at temperatures of the order of 100 million degrees.

## 7. Electrodeless Discharges

Let us assume that a high frequency, high voltage electric field is set up between two parallel, flat metallic plates, one or both covered with a thin dielectric of thickness  $d$  and one of them grounded. The electron avalanche generated with either metallic surface serving as cathode also generates large numbers of positive ions. The latter partially will recombine with the electrons to form neutral species but some will be left over when the direction of the current reverses and they cannot discharge on the dielectric except in three body collisions. Relatively high ionic concentrations are built up in the gas between the two plates and an appreciable degree of energy transfer may take place. The thicker the dielectric layers, the higher is the resistance they offer to the flow of electrons. However, without or too thin a dielectric arc discharges are formed more or less at random making the device useless for the purpose intended.

### A. Physical Characteristics of Electrodeless Discharges

In the operation of an electrodeless discharge, the relationships that occur between current, voltage, pressures, temperature and gas flow rate should be known in order to enable us to connect them up with the yields obtained for a given chemical system studied. Some measurements carried out by G.C. Akerlof (WADC Technical Report 57-189) for this purpose will be summarized in the following figures (Figures 5-9).

At constant current and active surface area, using an all glass reactor, it was found that an impressed voltage decreases linearly with increasing temperature. The resistance of a number of glasses decreases roughly by an order of magnitude per 100 degree temperature rise but the corresponding voltage drop is relatively small until temperatures well above

100°C have been reached. Similarly at constant current and temperature the voltage decreased linearly with increasing size of the activated surface area while it held constant when the gas flow rate was varied over a very wide range.

With respect to variations of the voltage with pressure and current, measurements made with several different gases are illustrated graphically in Figures 5-9. In the case of gases having relatively simple molecules which do not suffer extensive breakdown in the discharge, the curves shown reveal some very simple relationships. At constant current the voltage varies linearly with the pressure as demonstrated in Figure 5, using data for hydrogen. At constant pressure the voltage varies linearly with the current as shown in Figures 6 and 7 for a number of different gases with the exception of ethane and butadiene. Thus, in general, the slopes of the voltage-pressure curves must also vary linearly with the current as shown in Figure 8. These simple relationships do not hold for gases with polyatomic molecules like propane and butadiene, as illustrated in Figure 9, which rapidly form liquid products when exposed to the discharge. The current-voltage-pressure characteristics of mixed gases in electrodeless discharges would thus be dependent upon the reactions taking place between them.

Hysteresis in a chemical system may be defined as the lag in its approach to equilibrium. In a large number of cases the reactions taking place in an electrodeless discharge are propagated by a chain mechanism involving radicals generated by electron collisions with the molecules present. At finite reaction rates the attainment of steady state would require a certain length of time giving rise to hysteresis in the current-voltage curves when the power input to the discharge is varied. In the case of the system  $\text{TiCl}_4 + \text{C}_6\text{H}_6$  the hysteresis effect was found to be very pronounced with sharp inflection points for the value of  $\Delta I / \Delta E$ . With increasing voltage a lively chemical reaction seemed to be initiated when the inflection point was reached and to cease when it was passed as the voltage decreased.

B. Some Characteristics of Chemical Phenomena in Electrodeless Discharges

Mass spectroscopic studies have shown that when a hydrocarbon is exposed to an electron stream extensive breakdown of its molecules may occur under formation of a wide variety of free radicals, excited species and ions. As an example, Delfosse and Bleakney (Phys. Rev. 56, 208, 1939) found in a study of the behavior of propane, propylene and allene more than 60 separate ionic species, while Hipple (Phys. Rev. 53, 530, 1938) has shown that ethane generates fourteen different particles with a single and two with a double positive charge. The probability that an electron collision will excite rather than ionize a molecule will, however, increase with its size and degree of complexity. The relation between molecular structure and the amount of breakdown that occurs has been studied for a large number of different types of hydrocarbons by Linder and Davis (Journ. Phys. Chem. 35, 3649 (1931). They found that in the case of homologous series the amount of gas liberated per ampere-second increases with the molecular weight of the substance when it is exposed to a glow discharge. In Table 1 are given some data that illustrate this point.

Table 1. Gas Liberated by Various Hydrocarbons in a Glow Discharge According to Data of Linder and Davis

<u>Hydrocarbon</u>	<u>cc liberated per amp.-sec.</u>	<u>Hydrocarbon</u>	<u>cc liberated per amp.-sec.</u>
n-pentane	6.0	benzene	2.5
n-hexane	9.9	toluene	5.2
n-heptane	10.1	ethyl benzene	6.4
n-octane	10.5	n-propyl benzene	7.1
n-decane	11.3	n-butyl benzene	8.1
n-dodecane	13.3		

Similar studies employing electrodeless discharges have not appeared in the literature but it would seem probable that if undertaken they would, in general, have given the same result.

The theory of product formation in an electrodeless discharge is, as shown by the foregoing, an extremely complex problem involving a wide range of phenomena. An expression relating the rate of such reactions

with the gas pressure and the electrical factors describing the discharge has been formulated by Elliott, Joshi and Lunt (Trans. Faraday Soc. 23, 57, 1927). The fundamental idea is that the rate of the reactions would be associated with the number of collisions between ions and gas molecules in which the energy of the ion is equal to or exceeds a definite initial value. This value may be regarded as the critical energy of activation associated with the particular reaction concerned. According to the collision theory of chemical reaction, the rate of chemical change in a gas is a function of the kinetic energy of the constituent particles and it is immaterial whether the kinetic energy is of thermal or electrical origin.

As discussed above, when a gas is exposed to an electric field the energy acquired by the ions present increases with the field strength. When this energy begins to exceed a certain critical value known as the ionization potential new ions are produced by collision and the number of charged particles in the gas increases. When this takes place the electrical conductivity of the gas also increases. According to classical kinetic theory, the number of collisions  $c$  of an ion per unit length of its path which terminate free paths equal to or longer than  $X_c$  is given by the equation:

$$c = c_t \cdot e^{-V_o/\lambda E} \quad (1)$$

where  $c_t$  is the total number of collisions per unit length of path,  $V_o$  is the initial activation energy,  $\lambda$  the mean free path and  $E$  the field strength. The number of molecules reacting per unit time is thus equal to:

$$K = 2Nv \cdot c_t \cdot e^{-V_o/\lambda E} \quad (2)$$

where  $N$  is the number of ion pairs per unit volume and  $v$  is their average velocity in the direction of the field. Since the number of collisions per unit length of the path of an ion is proportional to the pressure  $p$  equation (2) may also be expressed as follows:

$$K = 2k.p. \cdot Nv \cdot e^{-V_o/\lambda E} \quad (3)$$

In order to apply equation (3) to experimental data, it is necessary to know the manner in which  $Nv$  varies with  $p$  and  $E$ . Since the composition of the gas starts to change immediately the discharge is initiated  $Nv$  and  $\lambda$  will also vary with time.

The current  $I$  carried per unit surface area of an electrodeless reactor may be expressed by the equation:

$$I = (U_+ + U_-) \cdot Ne \quad (4)$$

where  $U_+$  and  $U_-$  represent the velocity of the positive and negative ions respectively in the sustaining field  $E$ . Setting  $I = 2vNe$ , where  $v$  is the average velocity of the ions, equation (3) may thus be written:

$$K = (k \cdot p \cdot I)/E \cdot e^{-V_o/\lambda E} \quad (5)$$

Substituting the mean free path in equation (5) it may finally be expressed in the form:

$$\log (K/p) = A + \log I - p \cdot B. \quad (6)$$

where  $A$  and  $B$  are empirical constants. So far an actual experimental test of this equation has not appeared in the literature.



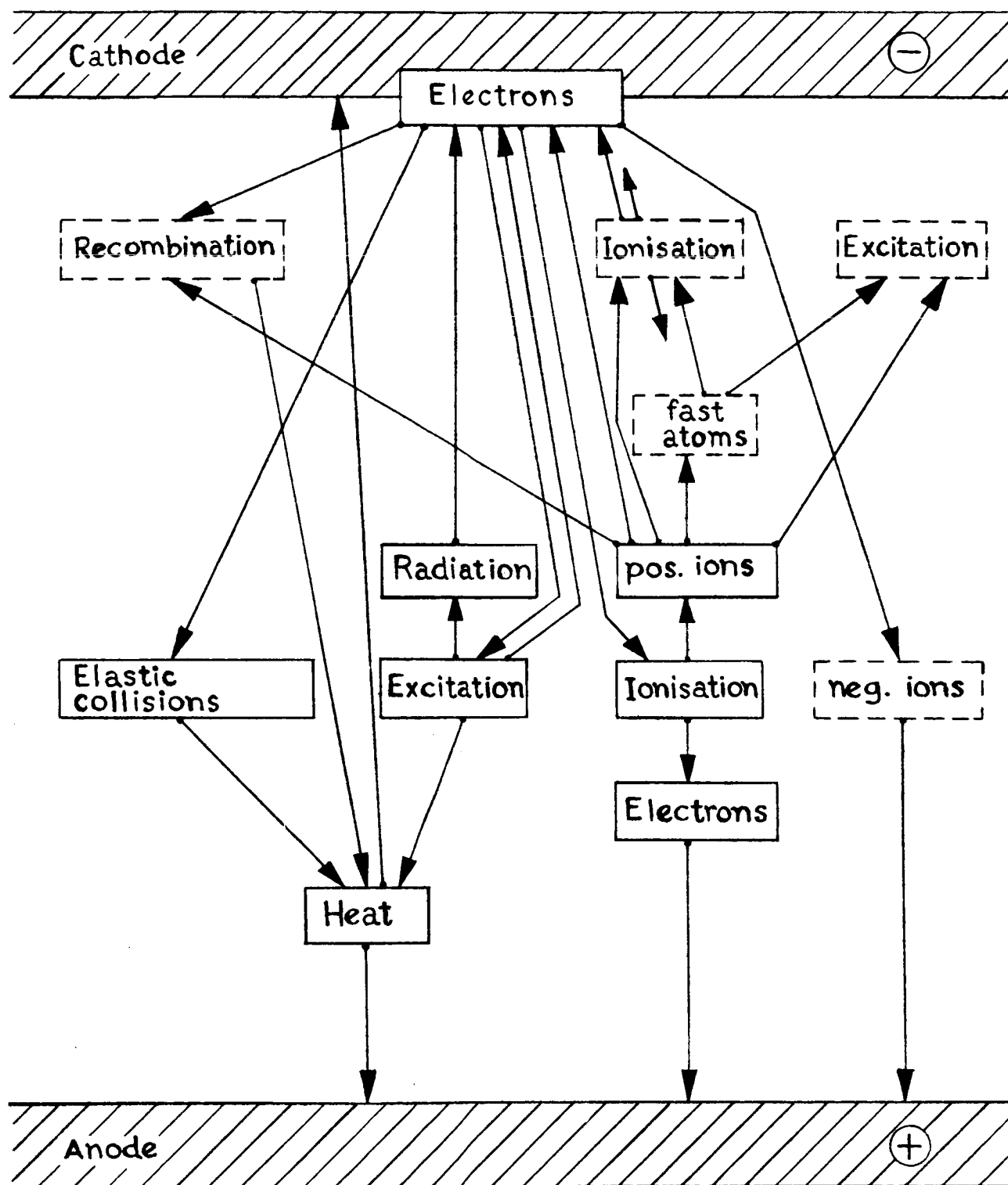


Figure 1. Elementary processes occurring in electric discharges. Each process is symbolized by an arrow. More important processes and particles are enclosed by a full line, others by a broken line.

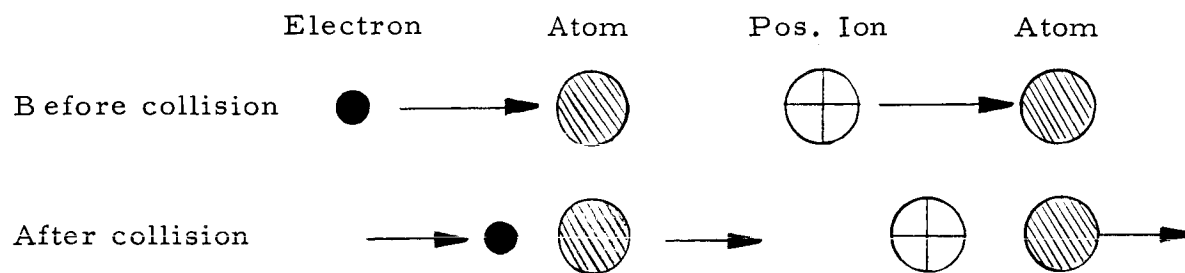


Figure 2. Central collision of electron with atom  
and of positive ion with atom

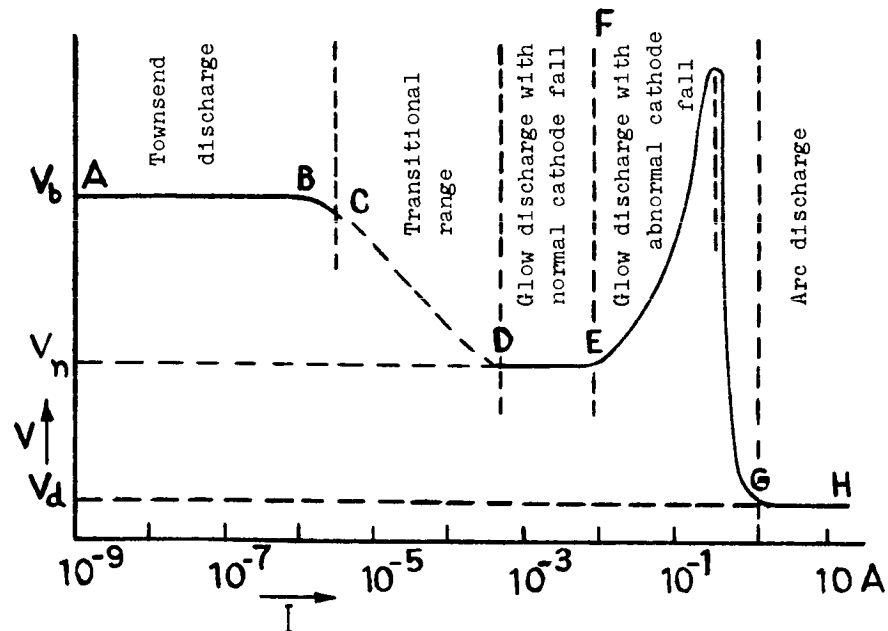


Figure 3. Schematic Diagram of the Characteristics of a Self-sustaining Gaseous Discharge. Voltage  $V$  on a Linear, Current  $i$  on a Logarithmic Scale

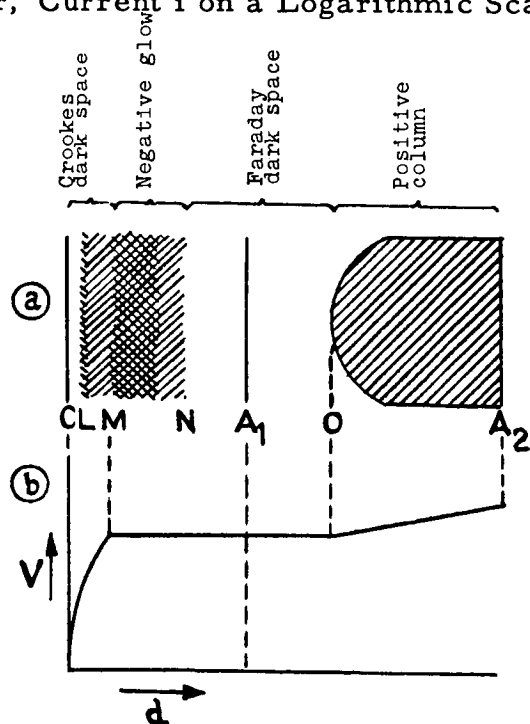


Figure 4. Glow Discharge Between Cathode C and Anode A at Two Different Positions of the Latter,  $A_1$  and  $A_2$

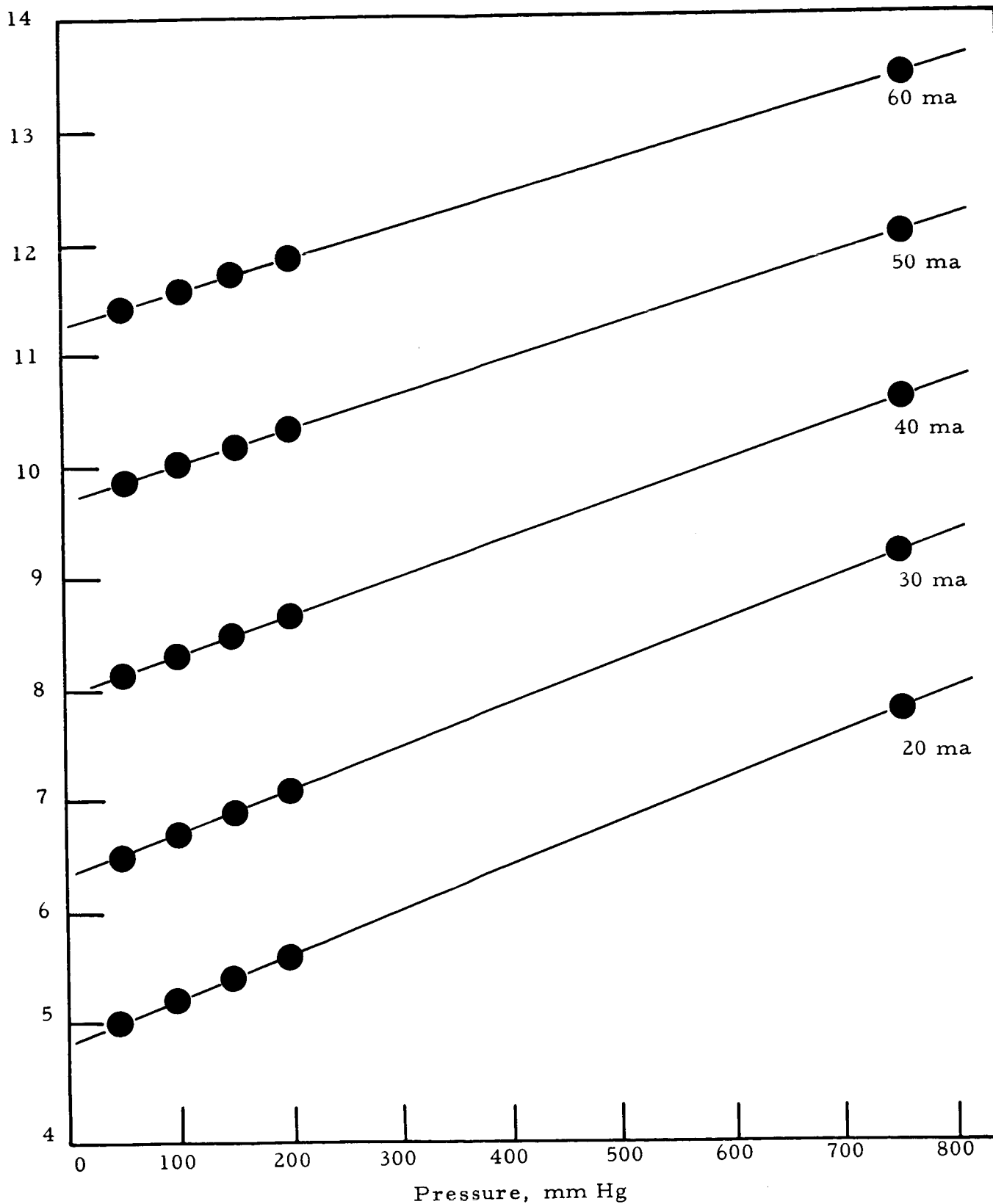


Figure 5. Reactor Voltage Variation with Pressure  
Data for Hydrogen Gas

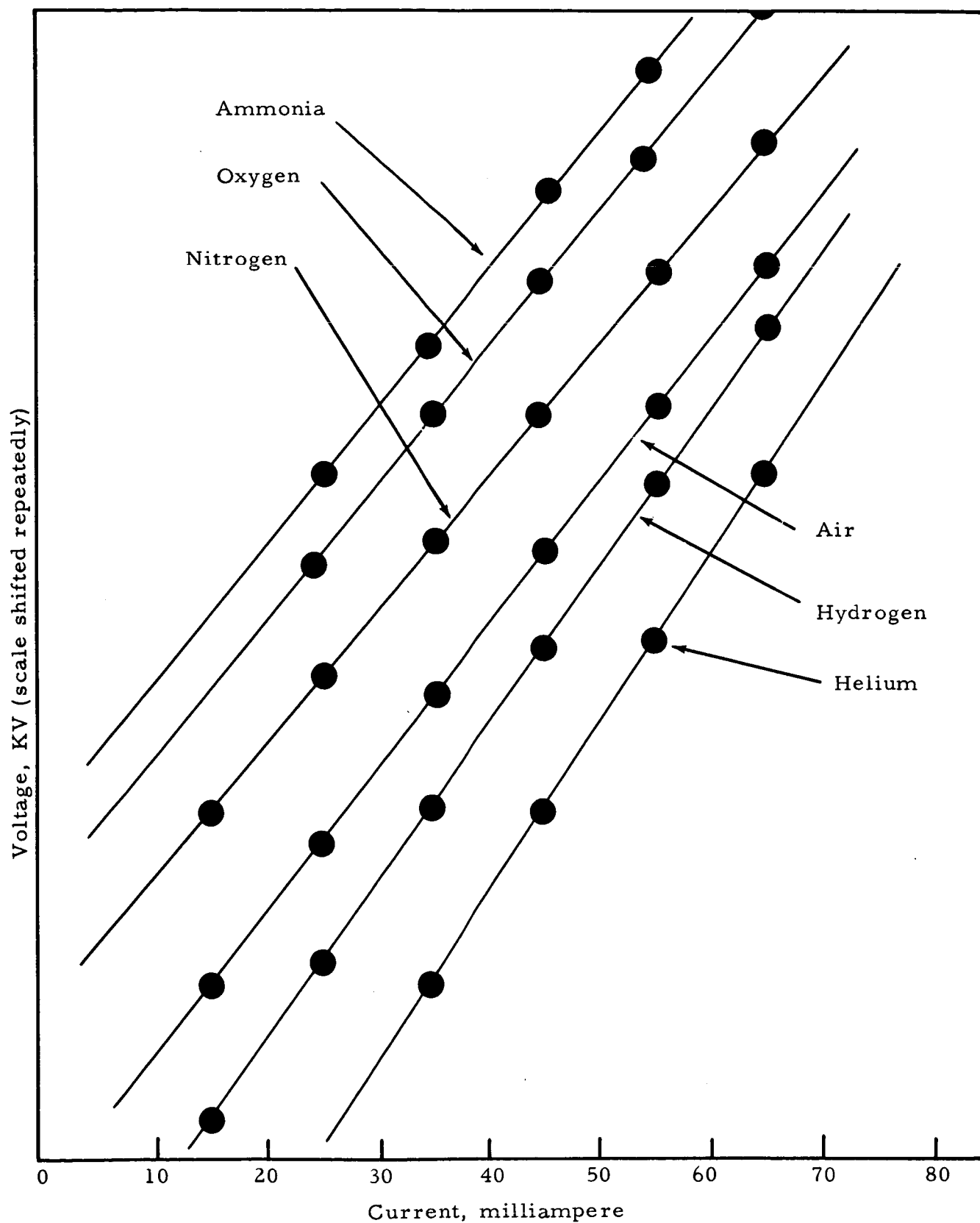


Figure 6. Reactor Voltage Variation with Current, Various Gases

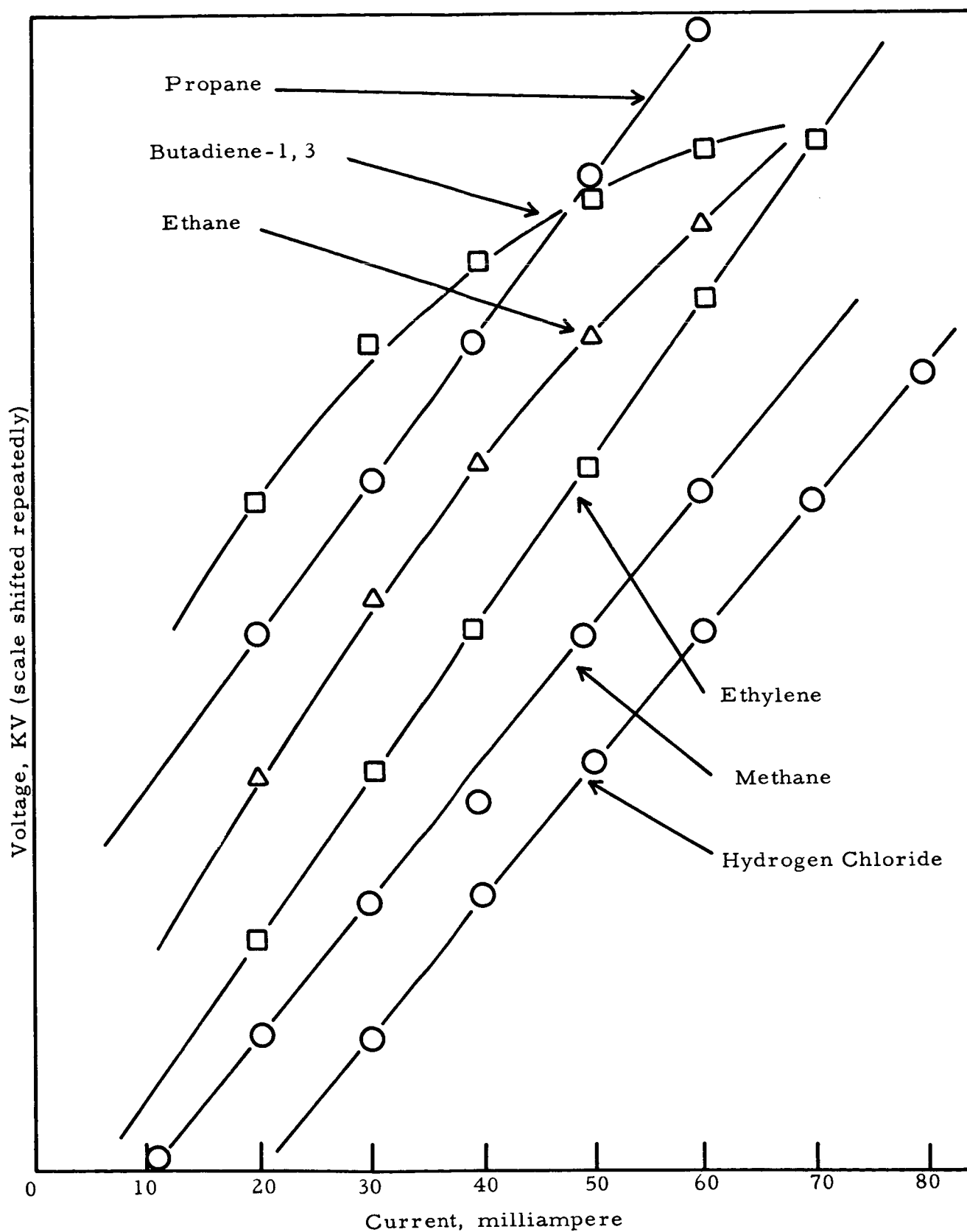


Figure 7. Voltage Variations with Current, Various Gases

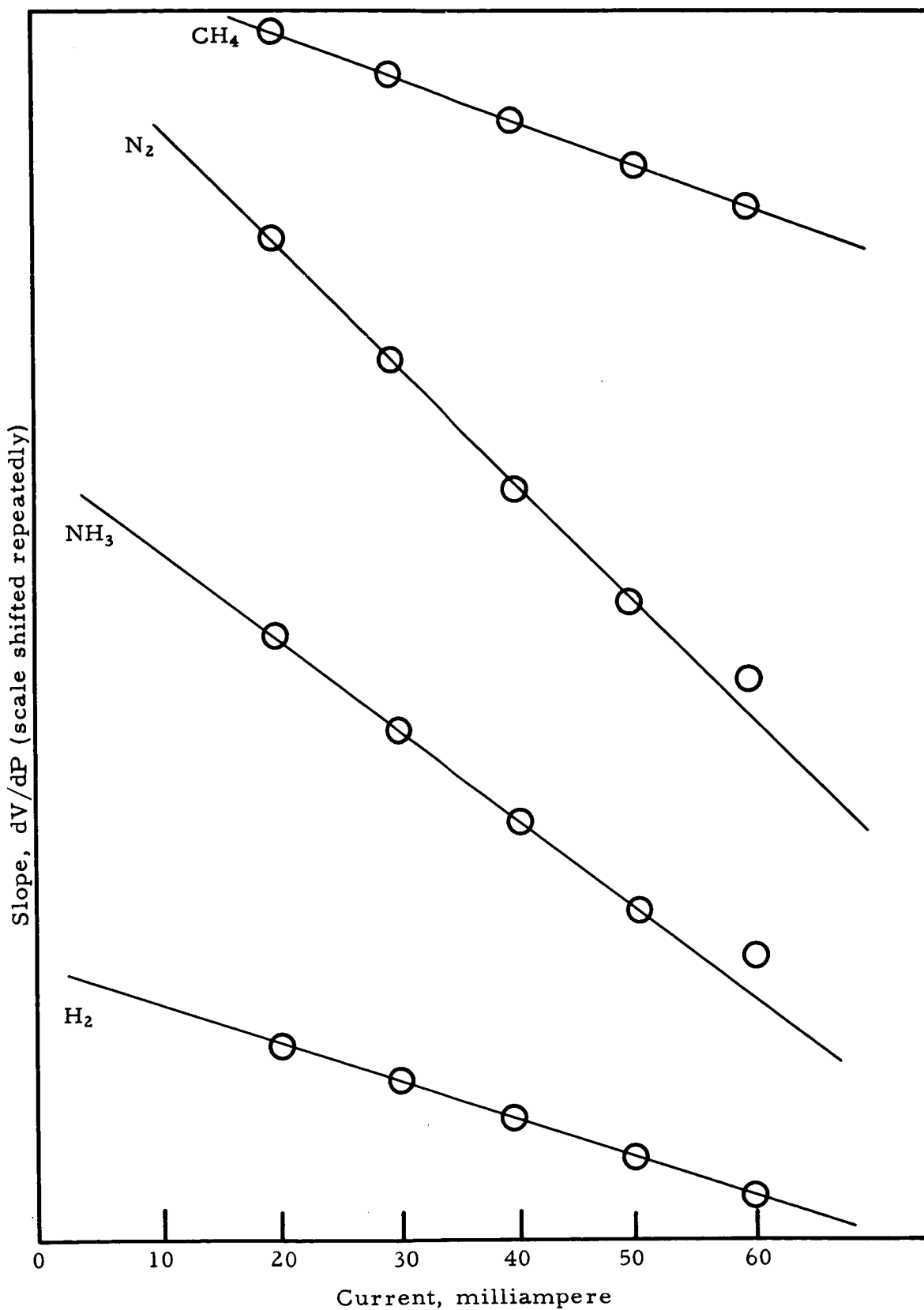


Figure 8. Slopes of Voltage - Pressure Curves for Several Gases

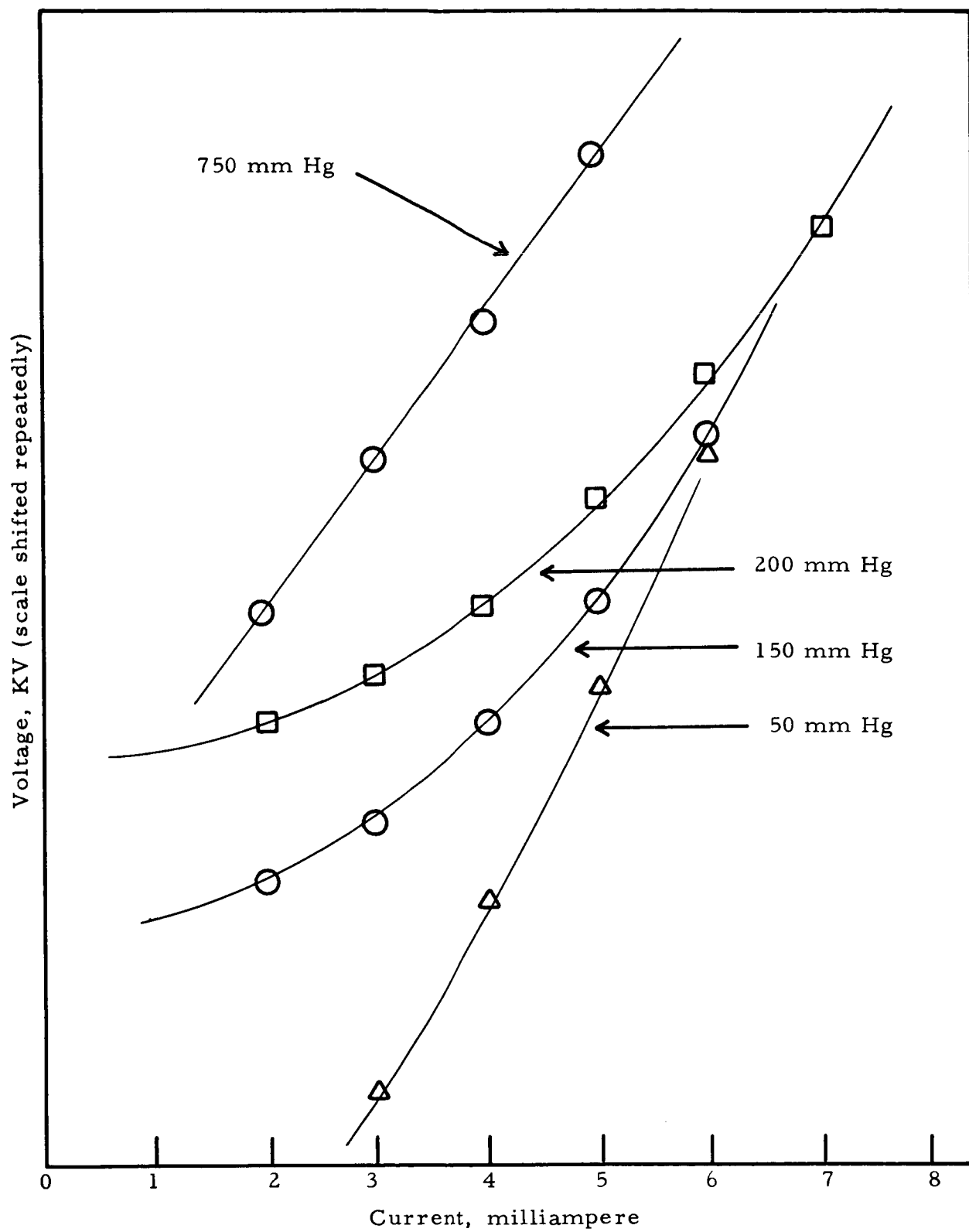


Figure 9. Reactor Voltage - Variation with Current at Several Pressures, Data for Propane



APPENDIX II

BIOLOGICAL TESTS

CONTENTS

- I. Key to Samples Tested
- II. Tests Carried out by Food and Drug Research Laboratories, Inc.
- III. Tests Carried out by Bio-Dynamics, Inc.

I. Key to Samples Tested

- |        |             |  |
|--------|-------------|--|
| (i)    | C-783-6     | Sugar mixture prepared by batch process from formaldehyde and $\text{Ca}(\text{OH})_2$ . The solution was deionized by a mixed bed resin before evaporation. |
| (ii)   | C-783-44    | The first sample prepared by the continuous process.   |
| (iii)  | C-783-73    | Prepared by the continuous process but with the "Tygon" spiral replaced by a glass spiral.   |
| (iv)   | C-783-88    | Prepared by the same method as in (iii).   |
| (v)    | C-783-121-1 | Material precipitated by ether from a 95% ethanolic solution of (iv).  |
| (vi)   | C-783-121-2 | Material remaining in solution after the removal of (v).   |
| (vii)  | C-710-97A   | First low molecular weight fractions from column chromatography of (iv).   |
| (viii) | C-710-97B   | The middle fractions obtained as in (vii).   |
| (ix)   | C-710-87    | The middle and highest molecular weight fractions of (iv) obtained as in (vii).  |
| (x)    | C-710-91-2  | Material precipitated by ether from a 95% ethanolic solution of (iv). (cf (v) above)   |
| (xi)   | C-710-91-1  | Material remaining from (x). (cf (vii) above)  |
| (xii)  | C-710-96-1  | Material remaining in an aqueous solution of (iv) after extraction of it continuously with ether for two weeks.  |
| (xiii) | C-710-100   | The first sample of synthetic sugar prepared by the condensation of a 15 percent aqueous solution of formaldehyde with lead oxide and sodium hydroxide.      |
| (xiv)  | C-710-100A  | A second sample prepared by the same method as in (xiii).  |

## II. Tests Carried Out by Food and Drug Research Laboratories, Inc.

### A. Utilization of C-783-6 by Yeast

This report describes experiments conducted to determine whether a substance identified as C783-6 was capable of serving as a carbon source for the growth of yeast.

#### Preliminary Tests

In the first experiment, a 1 percent solution of the sample in Czapek-Dox medium to which had been added 0.1 percent of yeast extract was inoculated with a suspension of Saccharomyces cerevisiae after sterilization by autoclaving at 15 lb. pressure for 15 minutes. The flasks containing the inoculated media were incubated at between 25 and 27°C on a rotary shaker for 48 hours. Comparable inoculated flasks contained the same medium with 1 percent sucrose. Uninoculated controls were also run at the same time. While it was apparent that growth was occurring both in flasks containing the sample and the sucrose, quantitative readings were difficult because of the different degree of darkening produced by the autoclaving process. The test sample appeared to be more susceptible to the effects of heat in this regard than was sucrose.

The experiment was therefore repeated in exactly the same manner except that the sterilization was accomplished by Zeitz filtration prior to inoculation. After 48 hours, the contents of the flask were read in a photoelectric turbidimeter, setting the uninoculated controls equal to 100 percent transmission. With sucrose as a source of carbon, the yeast gave a transmittance reading of 58 percent whereas the test sample permitted a growth equivalent to 70 percent transmittance.

These results warranted the conclusion that while the test material did support some yeast growth, it was not equivalent to sucrose.

#### Quantitative Evaluation

In this experiment, a series of 250 ml Erlenmeyer flasks were set up to contain graded concentrations of reagent grade glucose (anhydrous) in 25 ml of Czapek-Dox medium enriched with 0.1 percent yeast extract. The glucose concentrations were 0.1, 0.25, 0.50, and 1.0 percent. Sterilization was by autoclaving.

The test sample was prepared as a 13.8 percent solution (achieved after prolonged shaking at room temperature) which was sterilized by Zeitz filtration. Aliquots of the sterile solution were transferred aseptically to previously autoclaved basal medium in amounts of 0.5, 1.0, 1.5 and 2.0 ml with the total volume in each case making up 25 ml. Each series of flasks was then inoculated with one drop of a heavy yeast suspension per flask. Incubation was on a rotary shaker at 25°C for five days.

The transmittance of the incubated yeast cultures was then determined and the results obtained for the glucose plotted as a curve of transmittance versus concentration. The glucose equivalent of the test sample was then read from this standard curve. The data are summarized in Table 1.

#### Conclusions

Examination of the data shows that the response of the yeast to the test sample was considerably less than expected, although a definitely graded effect was demonstrated. By extrapolation of the response curve it can be estimated that 12.5 mg of glucose was approximately equivalent to 276 mg of the test sample which is a ratio of 22:1. Thus, C-783-6 may be said to possess 4.5 percent of the activity of glucose for yeast growth.

Table 1. Growth of Yeast

<u>Glucose</u>		<u>Sample C-783-6</u>	
<u>Concentration</u> <u>mg/25 ml.</u>	<u>Transmittance</u> <u>percent</u>	<u>Concentration</u> <u>mg/25 ml.</u>	<u>Transmittance</u> <u>percent</u>
0	100	0	100
25.0	50	69.0	92
62.5	28	138.0	85
125.0	18	207.0	79
250.0	15	276.0	73 <sup>1</sup>

<sup>1</sup> Since 276 mg of C-783-6 was approximately equal in promoting yeast growth to 12.5 mg of glucose, by interpolation, the test sample was 4.5 percent as active as the standard

B. Utilization of C-783-44 and C-783-73 by Yeast

This report covers preliminary tests on two samples of synthesized sugar mixtures to determine whether they would serve as normal metabolic sources of energy for the growth of yeast (Saccharomyces carlsbergensis). The first sample, C-783-44, consisted of a light brown viscous syrup. The second sample, C-783-73, was also a very viscous syrup but somewhat lighter in color than the first.

Tests were conducted to investigate the ability of each of the submitted samples to support the growth of yeast when supplied to a simple medium as the only source of carbon. The samples were diluted in sterile distilled water at the rate of 10 gm per 25 ml of solution. Graded levels of these dilutions were added to Czapek-Dox medium containing 0.1 percent of yeast extract to supply biotin. The resulting solutions were sterilized by Zeits filtration to avoid any degradation which might have resulted from autoclaving. The sterile solutions were distributed to tubes (20 ml per tube) and inoculated with 0.1 ml of a vegetative suspension of Saccharomyces carlsbergensis cells. The tubes were then incubated at 25°C on a rotary shaker for periods ranging up to 6 days after which the amount of growth was measured in terms of turbidity determined by percent light transmission in an Evelyn photoelectric photometer. With each series of test samples, an equivalent series containing graded levels of dextrose was prepared and treated in an identical manner.

When the turbidity produced in the presence of the test materials was compared with that of the standard curve resulting from dextrose, it was found that Sample C-783-44 was equivalent to one-fourth as much dextrose, on a weight basis (uncorrected for the water content of the sample). In other words, 40 mg of the sample per tube were required to yield the same turbidity produced by 10 mg of dextrose.

In similar tests with Sample C-783-73, essentially comparable results were obtained at the 40 mg per tube level, the actual estimates being 20 percent that of dextrose, weight for weight. With this sample, it was further noted that higher dosage levels resulting in a proportionate inhibition of the yeast. Thus, at 100 and 200 mg per tube, the dextrose equivalency was 11 and 8 percent, respectively.

C. Feeding Trials with Rats on C-783-44 and C-783-73

Initially, it was proposed to employ the samples as the carbohydrate moiety of an otherwise complete, nutritionally adequate, diet for young rats in such a manner that the resulting growth rate could be compared with that produced by an equivalent amount of sucrose (AR Grade). This technique is frequently referred to as the "caloric evaluation test" as described by Oser and Melnick (1).

Trial 1

Groups of the rats are fed, respectively, the unsupplemented diet (Table 2), diets supplemented with four graded level of sucrose, and diets supplemented with two levels of the test samples. On theoretical grounds, the latter were expected to provide 6 and 12 calories per day and to fall on the mid-points of the dose:response curve for sucrose. Pairs of male rats were used at each level in order to conserve the samples. The rats ate only negligible amounts of the experimental diets containing C-783-44. At both levels of dosage, they developed severe diarrhea and anal irritation, and died within an average of 5 and 6 days, respectively, at the lower and higher dosage levels. The sucrose-fed groups showed normal responses, their growth being proportional to caloric intake. The sucrose groups were discontinued on the seventh day.

Trial 2

In a second attempt to apply this basic technique, instead of incorporating the sample in the diet, it was administered by stomach as an 80 percent aqueous solution. The responses of the rats were similar to that described above and the test was discontinued after 6 days.

Trial 3

Three young adult male rats weighing about 200 gm were used in this test. Their average daily voluntary intake of a nutritionally adequate laboratory chow was determined in a one-week period of feeding. During the second week they were each allotted 70 percent of that amount of basal

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- (1) Oser, B.L., and Melnick, D., a rat growth assay for the physiological availability of potential calories in foods, (Abstract) 11th Meeting American Chemical Society (April 1947)

diet. One rat received no supplement, one received a supplement of 7.5 percent of the normal intake as sucrose, and one received a 30 percent supplement as Sample C-783-44. (This ratio of the carbohydrates was predicated on the assumption that C-783-44 might have a caloric value one-fourth that of sucrose.) Although the test rat also developed diarrhea, it survived. All three rats made small gains in weight, namely 6, 16 and 18 gm, respectively.

#### Trial 4

Three male rats weighing about 100 gm were maintained on the laboratory chow, ad libitum, but instead of the normal water supply, were given a 10 percent solution of C-783-44. Their water intake was slightly subnormal but via it they consumed from 1 to 3 gm of the test material. However their voluntary food intake was reduced to about one-third normal, and all of the rats developed diarrhea. The above tests exhausted the supply of C-783-44.

#### Trial 5

Sample C-783-73 was tested in this trial, using the caloric evaluation procedure described in Trial 1. Four rats were fed at each dosage level. None of them consumed their full quota of diet. They all lost weight and developed bloated abdomens and diarrhea. The test was discontinued after 6 days.

#### D. Summary and Conclusions on Tests B and C.

On the basis of the experiments described in this report, it appears that both of the synthesized sugar mixtures submitted were essentially similar in biological behavior. Neither was palatable to young rats at the high levels required for caloric evaluation and both were somewhat toxic, producing diarrhea, anal irritation, abdominal bloating, and death when significant amounts were ingested. One strain of brewers yeast was able to utilize a portion of the mixtures for growth at rates approximately equivalent to 20-25 percent that of dextrose. This figure, however, is not meaningful in view of the graded inhibitory effects observed at higher dosage levels.

It is concluded that although the mixtures undoubtedly contained sugars which are normally metabolized by both animals and microorganisms, they also contain toxic substances whose identity is unknown at this time.

Table 2. Composition of Basal Diet for Caloric Evaluation Study

<u>Ingredient</u>	<u>Grams per Day</u>
Lactalbumin	2.00
Salt Mixture <sup>1</sup>	0.40
Vitamin Mixture <sup>2</sup>	0.14
Cottonseed Oil	0.20

<sup>1</sup> Hawk-Oser Salt Mixture No. 3, Practical Physiological Chemistry, Hawk, P.B., Oser, B.L., and Summerson, W., Blakiston, N.Y., p. 1375.

<sup>2</sup> Furnishing:  
Vitamin A, 40 units; vitamin D, 4 units;  $\alpha$ -tocopherol, 2.4 mg; menadione, 20 mcg; thiamine HCl, 86 mcg; riboflavin, 172 mcg; pyridoxine, 47 mcg; niacin, 7.2 mg; calcium pantothenate, 570 mcg; p-aminobenzoic acid, 358 mcg; inositol, 14.3 mg; choline chloride, 28.6 mg; liver concentrate 1:20, 3.6 mg; biotin, 0.14 mcg; folic acid, 0.14 mcg; cyanocobalamin, 0.14 mcg; cellulose powder, q.s. to 0.14 gram.



### III. Tests Carried Out by Bio-Dynamics, Inc.

#### A. Feeding Tests with C-783-44

##### 1. General

The material used for this evaluation was a viscous brown, sweet tasting syrup having an odor approximating that of brown sugar.

##### 2. Experimental

A balanced synthetic diet was prepared, based on established principles of rodent nutrition, in which the test material represented the total number of calories due to carbohydrate. The ratio of the components in this diet was as follows:

<u>Component</u>	<u>Weight (gm)</u>
Casein	18
Sample C-783-44	40
Salt Mixture	3
Agar	3
Lard	23
Water	136
Cod Liver Oil	1
Tocopherol	1
Vitamins	3

The agar, lard and water were heated until the lard and agar melted. The mixture was stirred to assure homogeneity, and the other components were added as the mixture was cooling. Upon cooling, the diet assumed a semi-solid texture which was easily handled.

Evaluation of the initial palatability of the diet was carried out by feeding 10 gm of the diet to each of three 250-300 gm albino rats. The palatability having been established, six weanling albino rats (Sprague-Dawley strain) were used in an attempt to obtain some measure of any biological effects caused by chronic ingestion of the test sample. One group of three weanlings (two males, one female) was fed the experimental diet for three days after which time the diet was expended. The other three rats were used a control group receiving none of the test material.

3. Results

a. Food Consumption and Growth:

The three adult rats used during the initial phase of this evaluation rapidly consumed the total amount of food provided (10 gm/animal). This was taken as a positive solution to the question of palatability.

The remainder of the diet (limited in quantity by the amount of sample submitted) was fed to three weanling rats over a period of three days. Food consumption data and body weights are recorded in Table 3.

b. Symptomatology:

Moderate to severe diarrhea was noted in all three weanlings fed the test material. No other signs of gross intoxication were immediately apparent.

4. Discussion

The weight loss observed in those weanlings fed the test material is of some significance in view of the normally rapid growth demonstrated by rats at this age (note values for the control animals given in Table 3). Since weight loss in the experimental weanlings was not due to lack of food intake, two possible situations, or a combination thereof, are presented.

The first assumption would be that the test material had little or no caloric value. Consequently, protein and fat components of the diet would be preferentially metabolized to restore the caloric deficit. Utilization of dietary protein for restoration of caloric requirements would restrict the availability of these proteins for contributing to the general metabolic "pool" of amino acids. As current concepts of amino acid metabolism dictate that from this pool are drawn the amino acids necessary for synthesis of body protein, a decreased contribution on the part of dietary proteins could account for the observed growth decrease.

A second possibility, supported by the occurrence of moderately severe diarrhea, is that there is some order of toxicity attached to chronic ingestion of the test material. This could be due either to a major component of the sugar mixture or to some trace impurity.

The possibility also exists that the apparent growth retardation is due to a combination of both calorie deficit and toxicity. This latter premise is the most probable insofar as it is not likely that removal of carbohydrate calories would cause marked growth inhibition in such a short period of time.

5. Summary

- a. A balanced synthetic diet was devised in which the test sample represented the total number of calories due to carbohydrate.
- b. Three adult albino rats were used to demonstrate palatability of the diet containing the test material.
- c. Three weanling rats were fed the test diet for three days. Three additional weanlings were used as control.
- d. Loss of body weight and moderately severe diarrhea were recorded in those animals fed the diet containing the test sample.

Table 3. Body Weight and Food Consumption Data

	<u>Rat No.</u>	<u>Body Weight* (gm)</u>			<u>Food Consumption<sup>+</sup> (gm)</u>		
		<u>24</u>	<u>48</u>	<u>72</u>	<u>24</u>	<u>48</u>	<u>72</u>
		(hours)			(hours)		
Expt'l Animals	1 (M)	71	68	60	18	14	14
	2 (M)	68	64	59	19	13	14
	3 (F)	58	57	53	16	13	15
Control Animals	4 (M)	87	96	108	19	15	15
	5 (M)	79	85	95	20	15	14
	6 (F)	73	79	85	19	14	15

\* Weights taken following twenty-four hours feeding.

+ 20 gm fed the first day, and 15 gm fed for the second and third days.  
Values corrected for spillage.

B. Feeding Tests with C-783-88

1. General

The material used for this study was drawn from the sample of experimental sugar mixture, coded C-783-88. The sample, submitted for nutritional evaluation, was a viscous brown, sweet tasting syrup having an odor approximating that of brown sugar.

2. Experimental

The test material was incorporated into a balanced synthetic diet in such a manner as to represent the total number of calories due to carbohydrate. A second synthetic diet was prepared in which cellulose flour, having no caloric or nutritional value, replaced all carbohydrate calories. A third diet containing a normal compliment of carbohydrate calories was used as a control. The amount of the various components in each diet is recorded in Table 4.

Thirty weanling albino rats (Sprague-Dawley strain) were randomly divided into three groups of ten. Each group contained five male and five female rodents. One group was fed a diet containing the test material, a second fed a diet containing cellulose flour, and the third group fed the control diet. Animals in each of the three groups were weighed daily and the food consumption likewise noted. The duration of the experiment was eight days.

3. Results

a. Food Consumption and Growth:

Growth curves for each of the three feeding groups are presented in Figure 1. The experimental findings are further treated in Table 5.

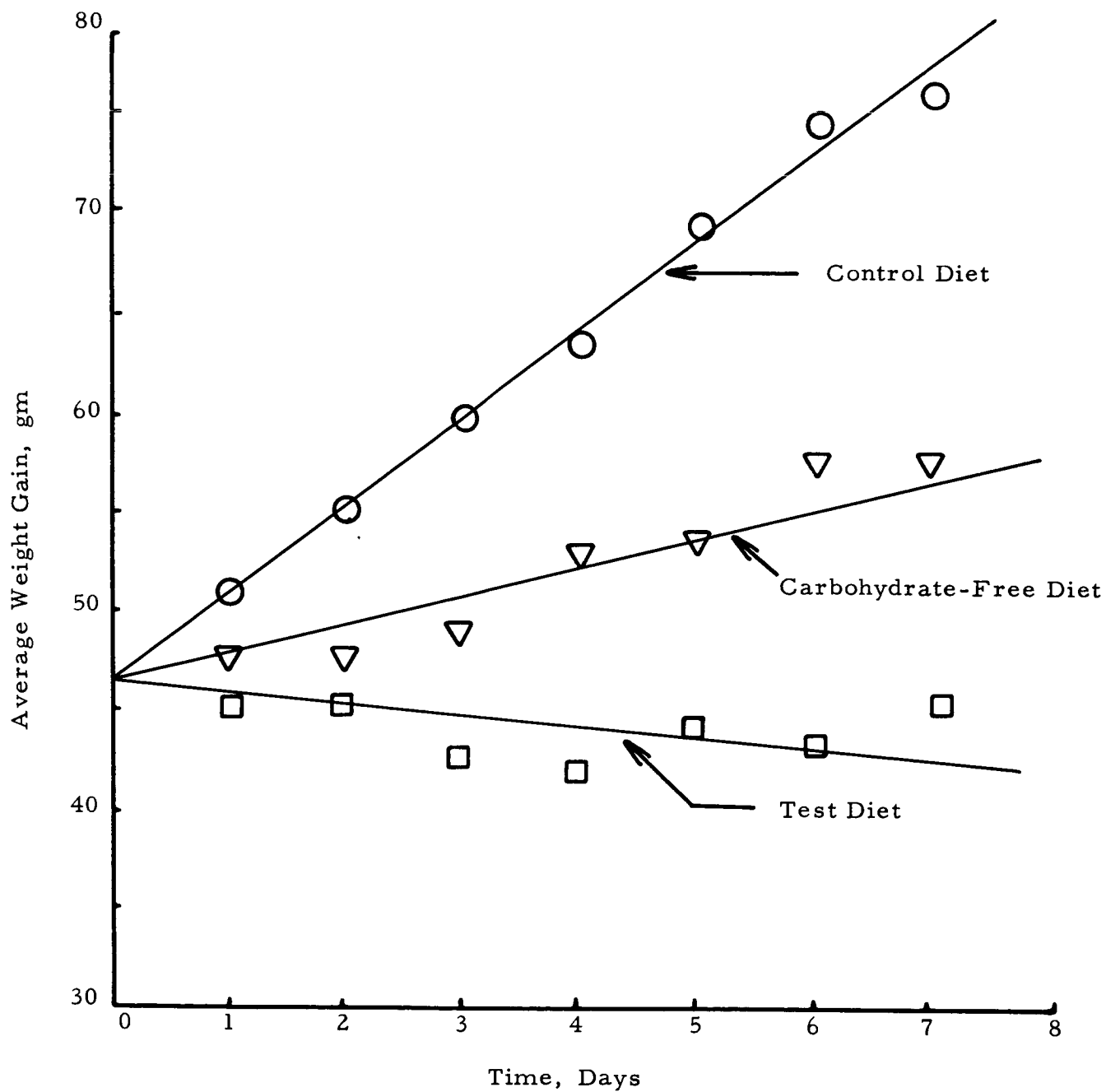


Figure 1. Growth Curves Corresponding to Ingestion of Three Classes of Synthetic Diets in Rats

Table 4. Composition of Basal Diet

<u>Ingredient</u>	<u>Diet A</u> (Control)	Am't (gm) <u>Diet B</u> (Carbo. free)	<u>Diet C</u> (Test)
Casein	180	180	180
Sucrose	134	-	-
Dextrose	202	-	-
Dextrin	159	-	-
Salt Mix	40	40	40
Agar	33	33	33
Lard	232	232	232
Water	1375	1375	1375
Cellulose	-	495	-
C-783-88	-	-	495
$\alpha$ -tocopherol in Crisco	10	10	10
Cod Liver Oil	10	10	10
Rodent Vitamins*	25	25	25

<u>*Rodent Vitamins</u>	<u>gm/liter</u>
Thiamine	0.192
Ascorbic Acid	0.384
Pyridoxine	0.154
Calcium Pantothenate	3.840
PABA	3.840
Riboflavin	0.307
2-methyl napthaquinone }	0.019
Vitamin K	
Biotin	0.019
Folic Acid	0.019
Inositol	9.600
Choline Cl	8.600

$\alpha$ -tocopherol is 10 gm in 1000 gm of Crisco

Table 5. Group Averages for Weight Gain, Food Consumption, and Food Efficiency

	<u>Total Wt. Gain (gm)</u>	<u>Total Food Cons. (gm)</u>	<u>Food Eff. **</u>
Diet A (Control)	30.0	125.8	0.24
Diet B (Carbo. free)	10.8	129.8	0.09
Diet C (Test)	1.0*	86.0	0.01

\* This value represents the average of a terminal weight gain in five animals and a loss in three. The average, being terminal, does not include those animals which failed to survive the duration of the experiment.

\*\* Food Efficiency = gm gain/gm food consumed.

b. Symptomatology:

Moderate to severe diarrhea was common to all animals fed the diet containing Sample No. C-783-88. This symptom was not observed in the other two groups. Abdomens of these animals were observed to become increasingly distended over the progress of the experiment. By the eighth day two animals had died and the survivors were noticeably smaller than those animals fed the other diets. In addition, their coats were rough and abnormal in appearance.

The only apparent difference between the control group and rodents fed the cellulose diet was a decreased growth rate in the carbohydrate free diet group.

Following the eighth day, three of the eight survivors in the test group were sacrificed and taken for gross autopsy. The remaining five animals were placed on a regular laboratory diet and continued under observation. All five of these animals died within three days of the end of the experiment. Post mortem examination of these animals, as well as those intentionally sacrificed, all demonstrated stomachs grossly swollen with what appeared to be undigested food. Further, several of the animals had a portion of their small intestines occupied by this same material.

4. Discussion

The experimental findings indicate the sugar mixture used for this study to have a toxic component (or components) which thus precludes evaluation of its nutritional value. The death of animals fed the test diet, as well as their prior condition compared to animals on the carbohydrate free diet, clearly demonstrates that the systemic stress noted is due to more than a caloric deficit. Post mortem examination, having revealed marked distension of the stomach by undigested food, suggests the possibility that the test material has the capacity to inactivate gastric enzymes responsible for partial digestion preceding passage of food into the intestine. In addition, the presence of undigested food in the beginning of the intestines suggests incapacitation of intestinal enzymes as well.

It is interesting to note that, while food consumption was higher in animals fed the carbohydrate free diet as compared to controls,



the gain in weight was only a third as great. This fact is reflected in a food efficiency of 0.09 for the carbohydrate free diet as compared to a value of 0.24 for the control. Examination of these ratios demonstrates the effects due to metabolic diversion of a portion of the dietary protein to aid in repairing a deficit in normal caloric requirements. Comparison of the 0.09 figure to the .01 efficiency obtained from feeding the test material shows this material to be nine times less efficient in promoting growth. Such a finding can be explained only on the basis of systemic pathology, which masks whatever food value might be intrinsic to the test material.

5. Summary

a. Three classes of synthetic diet were prepared. In one, Sample No. C-783-88 represented the total number of calories due to carbohydrate. The second diet utilized cellulose powder in place of carbohydrate, while the third contained a normal compliment of carbohydrate calories.

b. Feeding the test compound produced pathology, eventually leading to death, that could not be explained on the basis of a caloric deficit.

c. Sample No. C-783-88 is concluded to have a toxic component (or components) which precludes evaluation of the material's nutritional value.

C. Effect of Formaldehyde in the Diet

Formaldehyde was added to a complete synthetic diet as 4 mg free formaldehyde/gm of exp. sugar. Four weanling rats were fed the diet for five days. Slight weight loss was recorded, no other systemic effects were grossly observable.

D. Effect of C-783-88 on Adult Rats

The complete sugar mixture was incorporated into a synthetic diet, C-783-88, and fed to four adult albino rats. Massive diarrhea was noted following the first day and continued through the fourth, after which the diet was expended.

E. Feeding Tests with C-783-121-1 and C-783-121-2

Two portions of the complete mixture were intubated into two groups of weanlings, each group containing four animals. Two animals of the first group received 4 gm of C-783-121-1 as a 70% aqueous solution, and the remaining two received 4 gm of C-783-121-2, also as a 70% solution. In the second group of four weanlings, two animals received .21 gm. of C-783-121-1 as a 70% aqueous solution, and the remaining two animals received .21 gm of C-783-121-2.

Animals receiving 0.21 gm. have thus far demonstrated no observable toxic effects. Animals receiving 4.0 gm. have demonstrated the same symptoms of toxicity experienced with previous work done on the complete sugar mixture. There was, however, a difference in the time of the onset of symptoms between animals intubated with 4 gm of C-783-121-1 and C-783-121-2. The animals receiving C-783-121-1 did not present diarrhea and abdominal swelling until approximately 10-15 hours after C-783-121-2.

F. Feeding Tests with C-710-97A, C-710-97B, C-710-87, C-710-100, C-710-100A, C-701-91-1, C-710-91-2 and C-710-96-1

1. A screening technique was devised for rapid evaluation of new sugar mixtures in terms of systemic intoxication. This method involved administration of the sugar mixtures by stomach tubes of varying diameters, depending on the size of the rodents used. The animals used for these tests were Sprague-Dawley strain albino rats, and the sugars were administered as 80% aqueous solutions such that the animals received two grams of material/intubation. With Sample No. C-710-87, however, the one animal employed received only 1.8 gm due to a limited supply of material.

In addition to the intubation technique, four samples were incorporated into a synthetic diet as previously described.

Previous experience with these sugar mixtures has shown massive diarrhea to be the first sign of the lethal toxicity occasioned

by their ingestion. Therefore, the onset of diarrhea was used as an "end-point" for these tests, both diet fed and intubated. As soon as a sugar produced severe diarrhea, it was dropped from the test series.

2. Results

a. Intubated Rats

<u>Diarrhea-Time of Onset (hrs)</u>	<u>Sample No.</u>	<u>Quantity Intubated (gm)</u>	<u>No. of Rodents</u>	<u>Time Intubated (days)</u>
16-18	C-710-97A	2	1	1
16-18	C-710-97B	2	1	1
16-18	C-710-87	1-8	1	1
10-20	C-710-100	2	2	6
10-20	C-710-91-1	2	2	1
10-20	C-710-91-2	2	2	1
10-20	C-710-96-1	2	2	1

b. Diet Fed Rats

<u>Diarrhea-Time (hrs)</u>	<u>Sample No.</u>	<u>Quantity Fed</u>	<u>No. of Rodents</u>	<u>Time Fed (days)</u>
16-18	C-710-100	15 gm/day	4	3
16-18	C-710-100A	"	4	3
13-17	C-710-91-1	"	2	2
13-17	C-710-91-2	"	2	2

c. Effect of C-710-100 and C-710-100 on animal weights

<u>Animal No.</u>	<u>At start of Test</u>	<u>After 24 hrs.</u>	<u>After 39 1/2 hrs.</u>	<u>After 65 hrs.</u>	
1	295	278	271	264	C-710-100A
2	250	238	237	242	
3	297	279	271	271	
4	219	202	213	212	
1	216	204	201	192	C-710-100
2	300	284	277	271	
3	226	212	210	205	
4	293	269	272	255	

3. Summary

All animals tested presented massive diarrhea following administration of the experimental sugar mixtures. Examination of the onset times of the diarrhea shows no significant difference between the various samples. Further, comparison of the results obtained by intubating the sugars, as opposed to diet feeding, shows no significant difference in the time for the first signs of systemic intoxication to appear.

These experimental findings indicate some toxic component, or components, to be common to all the sugars tested in this series.

It should be noted that the correlation observed between results obtained by intubation and diet feeding shows the former technique to be a satisfactory method for the rapid and economical evaluation of sugar mixtures of this type.